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MINERALOGICAL CONTENT OF MAINE SANDS IN RELATION TO MORTAR STRENGTH

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In the recent papers from this laboratory[1] we have attempted to bring to the reader's attention the central problems of the concrete industry as applied to highways and bridges. These problems are, we feel, dependent upon the variation of mortar strength from specimen to specimen and the causes underlying this variation. The preceding paper of this series shows that the sand's iron content is an important element in mortar strength. In this paper an attempt will be made to indicate the relation of certain mineralogical elements to this mortar strength.

Geological conditions, the topography and the climate of the State of Maine have made possible the distribution of many types of sands, many of which are of excellent quality to use in the manufacture of concrete. Sand is a resulting product due to the weathering, disintegrating or fracturing of large areas of rock. According to George H. Stone,[2] the general nature of the rocks of Maine is as follows:

"A small area of sandstone is found in the southeastern part of the state. With this exception the coast region is covered by granite, gneiss, mica and other coarse-grained schists, with small areas of syenite, diorite and other crystalline rocks. In the central part of the state, nearly parallel with the coast, is a long belt of slates and other fine-grained schists. Still farther north is a parallel belt of fossiliferous rocks—sandstones, conglomerates and limestones. Numerous knobs and ridges of granite rise in the midst of other rocks. . . . .Most of these rocks are tough and compact in structure and contain free quartz. . . ."

Just after the so-called ice-age, the glacier swept over the whole area of the state so that the resulting sands contain many types of rock particles. This heterogeneous character may be best shown by 100 Maine sands taken at random and classified for their geological material.[3] For these 100 sands,

98 sands contained quartz
89 sands contained quartz as the major constituent
71 sands contained feldspar
71 sands contained feldspar as the second constituent

49 sands contained sandstone
38 sands contained mica
27 sands contained slate
12 sands contained limestone
9 sands contained schist
6 sands contained shale
3 sands contained gneiss

This paper attempts to show quantitatively how the mineralogical character of Maine sands affect the resulting tensile strength of mortar briquettes composed of one (1) part of portland cement and three (3) parts of sand when tested at the age of 7 and 28 days.

Tables 1 and 2 below present these data. In each of these tables the

TABLE 1

A CORRELATION TABLE SHOWING THE RELATIONSHIP OF % GRANITIC TEXTURE WITH 7-DAY TENSILE STRENGTH UPON 248 MAINE SANDS

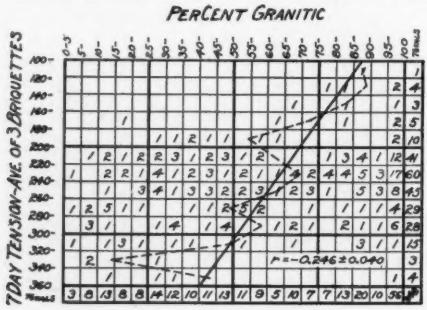
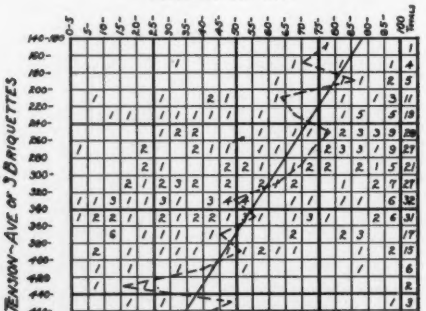


TABLE 2

A CORRELATION TABLE SHOWING THE RELATIONSHIP OF % GRANITIC TEXTURE WITH 28-DAY TENSILE STRENGTH UPON 248 MAINE SANDS



tensile strengths are plotted as ordinates and the "per cent granitic" as abscissae. The word "granitic" is here used to mean that portion of the sand that is either quartz, feldspar or mica, or combinations of those minerals which are primary in granite. The percentage basis is by actual weight as found on a small representative sample. The tension results are the average of three briquettes as expressed in pounds per square inch.

The irregular lines of tables 1 and 2 show the actual mean per cent of granitic materials for given 28-day tensile strength. The solid line shows the weighted average means for each strength. From these tables it is clear that as the amount of granitic material decreases the strength of the mortars increase. The correlation coefficients for this relationship are, for 7-day tensile strength, -0.246 ± 0.040. For the 28-day tensile strength the correlation is -0.337 ± 0.038. The correlation coefficients between granitic material and tensile strength increase with the age of the test specimens suggesting that the granitic material is more important to mortar strength the longer the mortar sets.

In 1923 a preliminary study of 318 sands showed a coefficient of correlation of -0.309 ± 0.020 between the 28-day tensile strength and the per cent granitic. This correlation checks nicely with that above. The sand was further separated into per cent of quartz and feldspar. The quartz content correlated with strength gave a coefficient of -0.317 ± 0.020, the feldspar content correlated with strength gave a coefficient of -0.294 ± 0.020. These results point to the conclusion that granitic material is detrimental to mortar strength and are in this sense a refutation of the commonly expressed belief that quartz sand is the best sand for the making of strong concrete. It also further suggests the fallibility of visual examination as a means of determining a good from a poor sand for use in concrete.

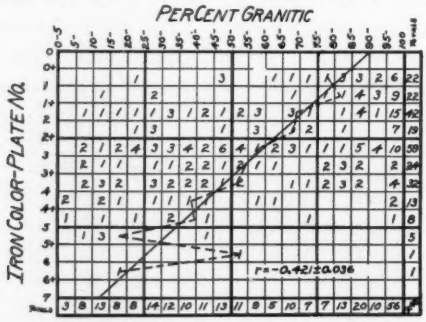
Our previous work on the importance of iron in mortar strength suggests the possibility that these small traces of iron may be intimately associated with the character of the sand as measured in terms of its granitic and non-granitic character.

Table 3 below shows the relationship between iron content and granitic content.

The coefficient of table 3 is -0.421 ± 0.036, which shows that there is a significant relationship existing between these two variables. The minus coefficient demonstrates that the non-granitic sands contain the most iron. The presence of iron in non-granitic sands explains in a measure their greater strength in mortars. The fact that a significant correlation of 0.27 ± 0.04 remains between the presence of iron and mortar strength with the percentage of granitic constant shows that both elements, percentage of iron and percentage of granitic material in the sand also play a part independent of each other in determining the strength of a mortar resulting from a given sand.

TABLE 3

A CORRELATION TABLE SHOWING RELATION BETWEEN IRON COLOR (A MEASURE OF IRON CONTENT) AND % GRANITIC TEXTURE ON 248 MAINE SANDS



Thus the amount of granitic material found in Maine sand has a relation to mortar strength such that the increase of granitic material results in a lowering of the mortar strength. The amount of granitic material is related to the amount of iron found in Maine sand, a large amount of granitic material indicating a low amount of iron. Part of the effects of the granitic material on mortar strength is accounted for by the lack of iron in the sand. There is, however, an independent relation as well, the iron content materially influencing strength even in sands constant in the amount of granitic materials.

[1] These PROCEEDINGS, **13**, 264 (1927).

[2] *U. S. Geological Survey*, **34** (1899).

[3] The writers are indebted to Dr. E. C. E. Lord, Petrographer of Bureau of Public Roads for this classification.

ON THE MECHANICS OF BLOOD FLOW, WITH SPECIAL REFERENCE TO THE INFLUENCE OF CHANGE OF POSTURE

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The recent development of reliable methods for determining total volume of blood flow in man, by Field, Bock, Gildea and Lathrop,[1] and by Henderson and Haggard,[1] adds a new and important measurement to the study of the mechanics of the circulation, comparable perhaps in significance to the discovery a generation ago of adequate clinical methods for blood-pressure determination.

With definite knowledge of these two factors, blood pressure and blood

flow, together with certain other data which are available, it should now be possible to examine problems of the circulation of the blood in man from a more strictly mechanical point of view than has heretofore been done.

We shall endeavor in the present paper to apply this point of view in a study of the effect of change of posture on blood flow.

It has long been known that in animals (except monkeys) the change from the horizontal to the vertical position is associated with a marked drop in blood pressure as well as a decrease in volume of flow. There is, for instance, the familiar experiment of holding a rabbit up by its ears, until the blood flow and arterial pressure reach the vanishing point, and the animal "bleeds to death into its splanchnic veins." The same phenomenon, to a less striking degree, occurs in dogs (Zybulski,[2] Friedmann[3] and Hill[4]).

Lindhard,[5] in 1913, was the first to measure in man the effect of change of posture on blood flow. Using Krogh and Lindhard's[6] nitrous oxide method, Lindhard found that of seven subjects, four (all men) showed practically the same flow and three (all women) a definitely smaller flow in the upright than in the recumbent posture. With the improved method (based on Fick's principle) developed by Field, Bock, Gildea and Lathrop, Field and Bock,[7] in determinations on thirteen subjects, found in every case a decreased flow in upright postures. There was an average decrease of 24 per cent in the sitting posture and of 50 per cent in the standing posture, as compared with the recumbent. These investigators also quote a series of determinations by Miss Turner, in which of 32 subjects in the sitting position, 17 had a smaller flow, 7 no change and 8 a rise, and of 19 subjects standing, 14 showed a smaller flow, 4 no change and one a larger flow. We have made several determinations in this laboratory on a small group of three subjects, using a method slightly modified from that of Field, Bock, Gildea and Lathrop, and have found the same changes as reported by Field and Bock, consistently lower blood flows in the sitting than in the recumbent position.

There thus appears to be in man a definite tendency for the volume of blood flow to be considerably decreased in upright postures—the same change that has been found to occur in animals.

Blood pressure changes in man in upright positions, as compared with recumbent, are, however, quite different from those found in animals. The literature on this point is somewhat confusing at first sight, because (1) some investigators have used supported vertical positions, and others these postures as maintained by the subjects themselves; and (2) some investigators have measured the systolic arterial pressures only, and others both systolic and diastolic pressures. With subjects supporting themselves in the standing position (which was the posture employed in the blood flow experiments of Field and Bock), and under normal external conditions,

the evidence is fairly conclusive that although the systolic blood pressure falls (Renquist[8]) the diastolic usually rises. The mean blood pressure, which is considerably nearer the diastolic than the systolic level, thus usually rises also, an average increase of 7 to 10 mm. Hg (Erlanger and Hooker,[9] Barach and Marks,[10] Hill,[11] Hill, Barnard and Soltau[12]). One must make exception, of course, of the situation in long continued experiments, where blood pressure falls considerably and symptoms of syncope supervene. There are also some individuals whose blood pressure will tend to fall even during brief periods in the standing posture. All studies agree in reporting decreased pulse pressure in the standing position. The pulse rate increases 10 to 50 per cent.

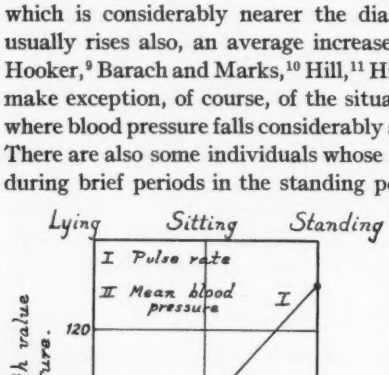

FIGURE 1

Changes in circulation with change of posture (Lawrence, Hurxthal and Bock). These figures, it will be noted, give somewhat lower percentage changes in blood flow following change of posture than those found by Field and Bock.

In the sitting position, the mean blood pressure shows little change from that in the recumbent. There is a tendency toward a slight fall in systolic and rise in diastolic pressures (Erlanger and Hooker). Pulse rate increases slightly.

Thus we have these conditions on changing from recumbency: (1) in the sitting posture, practically no change in mean blood pressure, and a decrease of 24 per cent in blood flow; (2) standing, an increase in mean blood pressure of 7 to 10 mm. Hg, a sharp decrease in pulse pressure, an increase of 10 to 50 per cent in pulse rate, and a decrease of 50 per cent in volume of blood flow.

The above relations between blood flow, pulse pressure and pulse rate have been fully confirmed in a very recent paper by Lawrence, Hurxthal and Bock.[13] The average figures obtained by these investigators on a series of ten normal individuals are presented diagrammatically in figure 1. The actual blood pressure figures, though not listed in this paper, have been made available for our use through the courtesy of Dr. Bock. The changes with change of posture are irregular, but show, on the average, fairly close agreement with the findings of earlier investigators with a tendency toward slightly lower pressure values in the sitting and standing postures. The average diastolic pressures show a fall of 3.5 per cent in the sitting posture, and a rise of 2 per cent in the standing, as compared with the recumbent. The systolic pressures fall 7 per cent in the sitting

and 12 per cent in the standing. Thus the mean blood pressure falls slightly in the sitting posture and remains practically constant in the standing; these data are also included in figure 1.

The explanation that has been offered for this marked decrease in flow in upright positions is that it is due to stasis or stagnation of blood in the veins of the viscera and lower extremities. The fact of accumulation of blood in these channels is, of course, apparent from ordinary observation. The effect of venous distension itself, upon volume flow of blood, has not, however, been inquired into in any detail; not even so far as to determine whether such distension would actually tend to decrease or increase the flow. In fact, no precise definition of "stasis," so far as we are aware, has been given. That is to say, it is not clear whether it means simply accumulation of blood in veins, without reference to the flow of blood, whether it means that the volume of flow is decreased, or the linear velocity of flow decreased, or whether there is assumed to be complete stagnation and immobility of blood in certain regions of the venous system.

Granting the accumulation of blood in the visceral and lower extremity veins in the upright position, one must inquire, inasmuch as practically the whole body is involved, into the source of this increased venous blood. Some undoubtedly comes from the partially collapsed veins of the head region, and some in all probability from the pulmonary circulation, the congestion of which in the recumbent posture is relieved in the upright on account of diminished flow of blood into the right heart. This proposition is suggested by Field and Bock in their discussion of the phenomenon of orthopnea. Mere venous distension, however, will not diminish blood flow. If the pressure gradients remain the same in a given system of tubes, the distension or enlargement of the tubes in one part of the system will cause increased flow due to diminished resistance.

For the brief period over which the blood flow is studied during posture changes, the total blood volume and blood composition are here taken as constant. Under these conditions, and with the mean blood pressure either the same or increased, a significantly decreased volume of blood flow can occur only by decreasing the cross sectional area of the channels of flow over one or more regions of the circulation, and this in turn only through (*a*) withdrawing or side-tracking blood from the active circulation, or (*b*) through a redistribution of blood between arteries and veins. We are here obviously disregarding the hydrostatic effects produced by gravity as the vertical posture is assumed. This is probably justifiable, however, because if (*a*) and (*b*) were both constant, the circulation would become a system of rigid tubes, and in such a system any effect produced by increase of hydrostatic pressure on the arterial side would be counterbalanced by an equal change on the venous side. Hürthle,[14] furthermore, in a paper to which we shall refer again presently, has shown that the

flow of viscous fluids in branching tubes is not appreciably affected by a varying arrangement and direction of the tubes with respect to the horizontal plane, such as occurs in the system of arteries, capillaries and veins.

If there is to be complete stagnation of blood anywhere in the venous side it will require either the draining of large amounts of blood into sinuses such as those of the spleen or the liver, with constriction of all other venous channels; or else, the actual stagnation of the blood in most of the branching venous vessels. The former possibility seems most unlikely; with increased hydrostatic pressure the venous vessels could hardly do anything but dilate; certainly all visible venous vessels are dilated in dependent positions; and the latter possibility can occur only if exactly equal pressures exist along all parts of the given stagnant sections of the venous system or if such sections are actually closed off by constriction at their proximal ends. The first of these hypotheses is impossible in a regularly branching system, and the second impossible in the existing venous system; that is, no vein of any size would close off against a positive pressure. The capillaries, moreover, contain only a small fraction of the total blood volume, and even they would not be likely to harbor appreciable amounts of stagnant blood; inactive capillaries, according to Krogh,[15] are empty. From computations that will be made presently, it will appear that in order to provide for a decrease of 25 per cent in volume of blood flow, about 62 per cent of the total blood in the venous vessels would have to be thus sidetracked—an absurd figure. Thus the "side-tracking" hypothesis is inadequate. The above argument is of course indirect, but necessarily so as we have not been able to find in the literature any measurements of active blood volume in varying postures.

There remains the second (*b*) of the alternatives, namely a redistribution of the blood in the lower part of the body, specifically a contraction of the arteries, and a corresponding dilatation of the veins. We believe that this is an important factor in the production of a decreased flow in the upright posture in man.

There is, of course, nothing original in the notion of such arterial contraction; one would naturally assume that contraction occurs, inasmuch as the mean blood pressure in the upright posture in man is either maintained or else actually increased over that in the recumbent posture. More specifically, the decreased pulse pressure, which is a constant finding in such a posture change, is what would be expected on the basis of lowered blood flow, increased pulse rate and contracted arteries: that is, the greatly diminished stroke volume will cause less distension of the aortic and larger artery walls, thus diminishing the systolic pressure, whereas the greater arterial resistance will increase the diastolic pressure. The increased pulse rate would itself tend to have the same effect of lowering the pulse pressure in the standing position. With such a pulse increase,

if the mean blood pressure is constant, one would expect a constant blood flow, supposing the peripheral blood vessels to remain unchanged; a large *decrease* of blood flow, however, could be associated with a constant mean blood pressure, irrespective of pulse rate, only if the arterial (or venous) resistance were increased.

This raises the question of the heart itself as a factor in the circulatory adjustment now under discussion. Cardiac output has been shown by Krogh[16] to depend largely upon venous inflow in such a manner that (*a*) when the inflow is "inadequate" and the auricular contraction is expended in filling an unfilled ventricle, the cardiac output is practically independent of rate of contraction; while (*b*) when the inflow is "adequate," and the auricular contraction is expended against a filled ventricle, causing a backward pulsation in the great veins, then the output is proportional to heart rate. Whether (*a*) or (*b*) obtains ordinarily in recumbent or upright postures in man is not known, but in either case the cardiac factor is not the dominant one; for if (*a*) obtains the heart rate makes little difference in the flow: while if (*b*) obtains there may be in upright postures some tendency toward a compensating increase of output from increased heart rate, but obviously insufficient, since the flow actually diminishes.

Direct experimental evidence of visceral arterial constriction in the upright posture was obtained as long ago as 1895 by Leonard Hill,[4] working with dogs and monkeys. Hill found that in dogs, although a shift from the horizontal to the feet-down position resulted in a certain fall in pressure in the carotid artery, this fall was less than would be expected from the change in hydrostatic conditions, a partial compensation being brought about through vaso-constriction in the splanchnic arteries (the condition of these vessels being determined by measurement of pressures in the splenic artery). In the experiments with monkeys, he found this compensation to be practically perfect; that is, the splanchnic vaso-constriction was so extensive as to maintain the carotid pressure practically unchanged in the feet-down position. In fact, in some monkeys the analogy to the condition in man was complete, there being a slight rise in carotid blood pressure in the upright position. In the splanchnic veins, as was to be expected, the change in pressure followed closely the changes in hydrostatic conditions. From Hill's work on these animals it appeared that most of the compensatory arterial constriction occurred in the splanchnic vessels, and relatively little in those of the lower extremities.

Assuming, then, that there is in the arteries of the viscera a contraction (whether in arteries or arterioles, or both, makes essentially little difference) resulting in a maintenance of mean blood pressure, and a redistribution of a corresponding amount of blood from arteries to veins, one must inquire what will be the effect on volume of blood flow. I think one can readily appreciate, qualitatively, that the blood flow will be diminished,

the increased pressure gradient in the arteries leaving a much lower gradient and, therefore, slower flow in the veins. The proposition can perhaps be more clearly stated as follows: in a system of circulating fluid flowing through first a narrower (arterial) set of tubes and then through a wider (venous) set of tubes, a contraction of the narrower set and corresponding dilatation of the wider, will result in a slower volume flow of fluid per unit of time, the pressure difference between the two ends of the system and the total volume of fluid remaining constant. This is obviously only a simple problem in maxima and minima, and its general truth can be apprehended at once. An approximate estimate of the relative quantitative changes in such a process as applied to blood flow, may, however, be obtained by a brief consideration of the conditions of flow of fluids in tubes.

The familiar law of Poisseuille, defining the flow of viscous fluids in cylindrical tubes, may be formulated as follows:

$$p = \frac{vl8\eta}{t\pi r^4}$$

where p = pressure, l = length of tubing, r = radius of tubing, t = time of flow, η = viscosity of fluid, v = volume of tubing = $\pi r^2 l$, v/t = volume of flow in unit time.

The law is derived on the basis of analogy between a viscous fluid and an elastic solid. That is to say, the fluid is considered as a material which is practically motionless at its outer surface, adjacent to the wall of the tube, and is elsewhere being "bent" in the direction of the fluid pressure, with the difference that adjacent particles are continually giving way and moving past one another in the direction of flow, instead of remaining fixed, as in the case of an elastic solid. Viscosity thus becomes analogous to elasticity in the mechanical sense.

The law depends, therefore, on homogeneity of fluid and smooth, stream-line motion of all parts of the fluid in the direction of flow, as two of the conditions of its applicability. There has been considerable doubt, for this reason, as to whether the law could be applied to the flow of blood in the blood vessels, the heterogeneity of the blood interfering in the smaller vessels, and eddy or vortex motions interfering in the larger ones. It was also doubtful whether the law could be applied to systems of branching tubes in both horizontal and vertical positions, or to a pulsating as well as to a continuous flow.

A critical study of this problem, both theoretical and experimental, was undertaken a few years ago by Hürthle.[14] He found the law to be closely applicable, at ordinarily existing pressures, to the conditions of flow in all blood vessels down as far as the capillaries, with the important exception of one condition, namely, that the variation in diameter of the vessels, occurring as a result of their elasticity and the pulsatile flow of blood,

disturbed the proportionality between pressure and flow. With increasing pressure, there is a more than proportional increase of flow, the discrepancy at normal blood pressures amounting to from 15 to 30 per cent. This discrepancy depends on a number of variable factors, and in further studies Hürthle[17] has not as yet been able to give an exact theoretical description of the relation in the vascular system between pressure and volume of flow.

In the present discussion, however, the pressure *changes* with change of posture are found to be slight, at least in the larger blood vessels where pulsatile variation in diameter is greatest, so that one may assume without gross error the applicability of Poisseuille's law to the flow in arteries and veins.

As far as the volume of blood and pressure changes are concerned, the capillaries are a relatively minor element, because in spite of their large total cross sectional area, and tremendous surface area, their average length is so slight—0.2 to 0.4 mm. (Krogh)—as to make the total volume of blood in them small, and the pressure loss negligible.

Since the available data, as given above, regarding changes of pressure and flow with change of posture represent only average and approximate measurements, it will not be profitable to attempt to use them for exact calculations of the effect of change of posture on the vascular system. We may, however, determine roughly the order of magnitude of such changes in the arterial and venous vessels. Assume as a first approximation that the mean arterial pressure remains constant. The capacity of the total systemic venous system is given by Hürthle[18] as about 80 per cent of the total blood in the systemic circulation or roughly four times that in the arterial system. Let us consider, for purposes of simplification, that the venous and arterial systems consist of single tubes, each of length l; the radius of the arterial tube will then be half that of the venous.

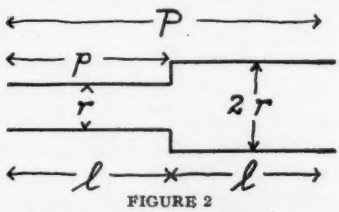

FIGURE 2
Schematic diagram of arterio-venous system.

Let r = radius of artery, $2r$ = radius of vein, l = length of venous and of arterial system, p = loss of pressure in arterial system, P = total loss of pressure = constant, $P - p$ = loss of pressure in venous system, V = volume of fluid = $\pi r^2 l + \pi(2r)^2 l$ = constant, f = volume of flow per minute through the system. Applying Poisseuille's law:

$$p = \frac{fl8\eta}{\pi r^4}, \qquad P - p = \frac{fl8\eta}{\pi(2r)^4}.$$

Adding and solving for flow:

$$f = 0.94\,\frac{\pi P r^4}{l8\eta}.$$

In order to diminish the flow to half this value, that is to $0.47\pi Pr^4/(l8\eta)$, keeping the total volume and total pressure loss constant, it can easily be computed that the arterial radius will have to be about 0.83 time its original value, and the venous radius 1.04 times its original value. Thus, applying this to the blood flow, one sees that the requisite decrease in volume of flow, in passing from recumbent to upright posture, is attained by an arterial constriction of only 17 per cent in radius, and a venous dilatation of 4 per cent. The important change here is, of course, the arterial contraction, the diminution in flow being almost the same without the venous dilatation.

It should be emphasized that the above figures are by no means intended as close approximations to the actual state of affairs in the normal circulation. They do indicate, however, that relatively slight changes in distribution of the blood between arteries and veins can cause considerable alteration in blood flow.

It can readily be seen from the preceding discussion that alteration in the caliber of the venous vessels will cause relatively little change in pressure or volume of flow. Thus supposing a venous distension such that the radius $2r$ in the diagram becomes $2.5r$, the total pressure loss remaining the same, but the total volume of fluid increasing, the resultant change is to increase the flow by about 3.5 per cent of its previous value. Similarly, if the venous channel is diminished, as by "side-tracking" of blood, this channel will have to be decreased to 38 per cent of its previous volume to cause a decrease in flow of 25 per cent, and to 24 per cent of its previous volume in order to cause a 50 per cent decrease in flow.

Our rough calculations, as stated, have assumed the mean arterial pressure to remain constant. In the standing position the pressure is often actually increased; there is also probably a tendency for blood flow to increase due to peripheral muscular contractions. These factors thus place an added burden, as it were, on the vasoconstricting mechanism, in its provision for a 50 per cent decrease in blood flow. Without accurate data, calculations are out of the question, but with the flow varying as the fourth power of the radius, one may presume that the method of arterial constriction will be sufficient to provide for the observed decrease in flow.

There is one other possible mechanism of adjustment of blood flow which should be mentioned. This was outlined by Krogh[19] in the series of papers referred to above, regarding venous supply to the heart. He demonstrated that in the portal system there exists a special mechanism for throwing an additional volume of blood into the rest of the circulation, by reason of the double set of resistances in this system, (1) intestinal arterioles, capillaries and venules and (2) liver venules and capillaries. It is on account of the latter that the portal vein pressure is about 25 mm. Hg whereas in other large systemic veins the pressure is only 5 or 10 mm. Hg. By

strong contraction of intestinal arterioles, the pressure gradient there can be increased, thus decreasing the pressure in the portal vein system, which thereupon empties itself more or less completely into the vena cava. The effect of this upon blood flow, according to Krogh, is an increase, by increasing the venous supply to the heart. Thus one would expect by this mechanism, a simultaneous increase of blood flow and blood pressure upon contraction of intestinal arterioles. It is clear, however, that no such adjustment occurs with change of posture, for although intestinal arterioles undoubtedly do contract with the body in the upright position, and blood pressure is maintained, the large hydrostatic effect increasing portal vein pressure will outbalance the other tendency to decrease this pressure, and these veins will, therefore, further distend and blood flow will diminish.

The present paper has been restricted to a consideration of the application of Poisseuille's law to a single simple physiological phenomenon. Other applications will suggest themselves. The relation, for instance, between linear velocity of blood flow and volume of blood flow becomes apparent; and the limitations within which these two measurements are proportional, or nearly so, can be easily worked out (cf. the work of Blumgart and Weiss[20]). This relation has been pointed out by Hürthle[18] but no application of the relationship demonstrated. There has been, in fact, with a few exceptions (Hürthle, Schleier,[21] Murray[22]) little application of the principles of Poisseuille's law to problems of the circulation, and perhaps for this reason a persistence in physiological terminology of such vague terms as "peripheral resistance" and "venous stasis."

This law, of course, does not apply exactly to the flow of blood in the vascular system, but with the exceptions noted above, the applicability is close, and if further studies can determine, even approximately, the pressure-flow relationship, one may venture the hope that general problems of blood flow, both physiological and clinical, may be dealt with in concepts that are more precise, and better founded on mechanical principles, than has heretofore been possible.

Summary.—The decrease in volume of blood flow in man on assuming the upright posture from the recumbent is shown to be associated with arterial constriction. The discussion is based on the application to the circulatory system of Poisseuille's law of flow.

[1] Field, H., Bock, A. V., Gildea, E. F., and Lathrop, F. L., *J. Clin. Inv.*, **1**, 1924 (65–85); Henderson, Y., and Haggard, H. W., *Am. J. Physiol.*, **73**, 1925 (193–253).

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[5] Lindhard, J., *Skand. Arch. Physiol.*, **30**, 1913 (395–415).

[6] Krogh, A., and Lindhard, J., *Ibid.*, **27**, 1912 (100–125).

[7] Field, H., and Bock, A. V., *J. Clin. Inv.*, **2**, 1925 (67–76).

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THE NATURE OF THE INSENSIBLE PERSPIRATION

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Read before the Academy April 25, 1927

The fact that all humans are continually losing weight, even when quiet or asleep, has been known since the days of Sanctorius in 1614. The quantitative relation between the size of the body and the loss in weight per hour has been determined, and the loss has been found to be larger with the larger person. Furthermore, physical activity, even if moderate, increases the loss.

The measurement of the insensible perspiration can be obtained with an inexpensive decimal balance, sensitive to 10 grams, by weighing the person just before going to bed at night and again in the morning upon rising. If due precautions are taken with regard to the inventory of clothing and accessories and the avoidance of any intake of food or drink, and if account is taken of any loss in urine or feces, the insensible loss is readily computed. This will amount to not far from 100 or 200 grams in an overnight rest. On a more delicate balance, sensitive to 0.1 gram, the periods of measurement may be as short as 15 minutes. Indeed, 4 or 5 consecutive 15-minute periods will almost invariably indicate a regular loss.

In the Nutrition Laboratory we have measured the insensible loss of a number of normal subjects, and in coöperation with Dr. Howard F. Root, of Dr. E. P. Joslin's clinic, measurements have also been made on diabetics and on toxic goitre patients from Dr. F. H. Lahey's clinic. Simultaneous metabolism studies gave the data for the comparison of the loss per hour and the metabolism. The relationship was found to be close, a low metabolism usually accompanying a low insensible perspiration. If the values

for the insensible loss per hour of the diabetic and goitre patients are plotted against the results for the computed 24-hour heat-production, a straight-line curve is seen to represent the general trend of the relationship. Indeed, all of our numerous normal data lie so close to this line that it is believed that this simple measurement of the insensible perspiration may serve as an excellent index of the total metabolism.

The nature of the insensible perspiration became of general interest when we found that the hourly loss was unaffected by disrobing or by a blast of air directed by an electric fan over the nude body. That water vapor is lost both from the lungs and the skin has long been known. That a certain small proportion of the total carbon dioxide lost escapes through the skin has also been demonstrated. But just what proportion of water vapor is lost from the skin and what proportion from the lungs, and how the carbon-dioxide loss and the oxygen intake balance each other are processes but little understood. Our first problem was to separate the loss from the lungs from the loss from the skin. To do this we have a subject lie on the balance and breathe into a simple closed-circuit respiration apparatus, which is *weighed on the balance with the subject.* A small tank or cylinder of oxygen is also placed on the balance. By closing the nostrils of the subject, the entire act of respiration can go on without affecting the body-weight, for oxygen from the cylinder passes into the respiratory tract and reissues shortly as carbon dioxide, which is collected and absorbed, as well as the water exhaled, in the soda-lime of the apparatus. Thus all the oxygen escaping from the cylinder is retained on the balance, either in the products of respiration or in the body. All the carbon dioxide produced is also retained on the balance. Any loss in weight of the subject plus the respiration apparatus must, therefore, be due exclusively to the skin loss.

The total insensible loss from the body may amount to from 20 to 30 grams per hour, but since the skin loss is only about one-half this amount, the period of measurement of the skin loss must be lengthened. Since this necessitates long retention of the mouthpiece, it is better to relieve the lungs of any work of opening and closing air valves and moving the air along the pipes of the apparatus by using a small electric blower, weighed also with the subject. The loss thus measured will be the skin loss only and, indeed, the whole of the skin loss. It must be emphasized that the high surface temperature of the face and forehead makes questionable the neglect of these surfaces in the determination of the loss from the skin. Hence if the subject is placed in a chamber with the head outside, the loss from this important water-yielding surface is not included.

The total loss is determined in a period preceding or following the measurement of the skin loss. A comparison of the total and the skin losses of 9 different subjects is given in table 1, from which it is seen that although

TABLE 1

THE TOTAL INSENSIBLE PERSPIRATION AND THE INSENSIBLE LOSS FROM THE SKIN ALONE

	GRAMS PER HOUR		
SUBJECT	TOTAL LOSS	LOSS FROM SKIN	PER CENT LOST FROM SKIN
I	27.3	19.2	70
II	18.2	8.1	45
III	60.6	21.4	35
IV	23.3	11.1	48
V	18.9	9.3	49
VI	26.1	12.9	49
VII	25.9	15.7	61
VIII	30.9	13.9	45
IX	34.0	17.0	50
Average			50

the proportion from the skin ranges from as low as 35 per cent to as high as 70 per cent, the average skin loss is 50 per cent of the total loss. One-half of the total insensible perspiration of a resting person may, therefore, be considered, on the average, to be from the skin and the other half from the lungs.

Employing as subject an artist's model, well-trained in metabolism experiments, we were able to study the effect of disrobing upon the skin loss. The room temperature during these experiments was usually about 20°C. and, singularly enough, it can be seen from table 2 that of the total loss the percentage lost from the skin was not especially different when the subject was nude than when she was clothed.

TABLE 2

INFLUENCE OF DISROBING ON THE INSENSIBLE LOSS FROM THE SKIN—MISS W. (AVERAGE ROOM TEMPERATURE, 20°C.)

		GRAMS PER HOUR		
EXPERIMENT	CONDITION	TOTAL LOSS	LOSS FROM SKIN	PER CENT LOST FROM SKIN
I	Nude	17.2	8.7	51
II	Nude	19.3	10.5	54
III	Nude	24.7	8.9	36
	Nude	17.4	8.9	51
	Nude	17.8	7.6	43
IV	Clothed	23.8	9.5	40
V	Clothed	19.3	10.1	52

Although the chief interest in the gaseous emanations from the lungs is normally in the carbon-dioxide production and the oxygen consumption, from the standpoint of heat loss the water vaporized from the lungs is of exactly the same importance as that vaporized from the skin. Hence our next problem was to analyze the insensible loss from the lungs, with particular reference to the relationships between the water vapor exhaled,

the carbon dioxide eliminated and the oxygen absorbed. Of further special interest was the relationship between the water vapor exhaled from the lungs and the water vaporized from the skin, for we can assume that the skin loss is comprised chiefly of water. To separate the products of respiration or the products of the loss from the lungs, a modification of the apparatus was necessary. In the apparatus used for the foregoing experiments both respiratory products, water vapor and carbon dioxide, were passed into a soda-lime can and there either absorbed or condensed. To measure each of these individually, the reagents must be in separate containers and the water vapor must be absorbed by passing the air from the lungs, first, into a weighed sulphuric-acid bottle and then into a weighed soda-lime bottle, followed by a second weighed sulphuric-acid bottle, all preferably suspended beneath the bed. Thus, in the first bottle the water vapor is absorbed quantitatively and in the next two bottles the carbon dioxide is absorbed. Oxygen is admitted, as before, from a cylinder on the balance, and a small expansion chamber with bathing cap is provided to give complete freedom in respiration. An electric ventilator moves the air, and respiration is free and even, permitting an experiment of an hour's duration. Under these conditions the loss in weight of the subject *and* the respiration apparatus suspended on the balance represents, as in the experiments with the other arrangement of apparatus, the skin loss. But by weighing the separate containers one can determine the water vapor given off by the lungs during the hour and the carbon dioxide exhaled, and by weighing the oxygen cylinder before and after the experiment one can find the amount of oxygen consumed. The air passing from the mouth is drawn into the sulphuric-acid bottle, and just before returning to the mouth, after being freed of carbon dioxide, it enters a small expansion chamber. The oxygen cylinder is attached to one of the chains supporting the bed, and connects directly with a petcock in the bottom of the expansion chamber. This apparatus permits a complete analysis of the insensible perspiration, for the total insensible loss may be determined in a preliminary period, and in a succeeding one-hour period one can simultaneously measure the skin loss, the water vapor exhaled from the lungs, the carbon dioxide exhaled from the lungs, and the oxygen consumed.

We have made numerous experiments, chiefly with one subject, in which the insensible perspiration has been analyzed by the scheme as outlined, and the effects of environmental temperature, of the removal of clothing, and of a blast of air from an electric fan have been readily determined. Thus, a typical experiment showed in the preliminary period a total insensible loss, both from the lungs and skin, of 21.76 grams per hour when the subject was nude in an environmental temperature of 25°C. In the next period, when the nature of the loss was studied, it was found that 7.58 grams per hour were lost from the skin, 8.13 grams were lost as water

from the lungs, 17.08 grams of carbon dioxide were eliminated, and 15.36 grams of oxygen were absorbed. In another experiment at a room temperature of 20° C. the total loss, when the fan was blowing over the nude body, was 19.55 grams per hour. In a period immediately following, with the fan still going, 8.45 grams were lost from the skin, 7.29 grams were lost as water from the lungs, 22.54 grams of carbon dioxide were eliminated, and 19.81 grams of oxygen were absorbed.

Although the data are too extensive to permit of presentation here and the various details cannot be discussed as fully as desired, an analysis of our data makes it clear that the loss from the skin, which may be considered to be a loss of water, is essentially the same as the water lost from the lungs, i.e., 8 grams per hour. The total insensible loss of this subject was not far from 20 grams per hour. Since the skin loss was 8 grams and the loss of water from the lungs was 8 grams, the total loss of water was 16 grams. The 4 grams unaccounted for are in large part made up by the difference between the weight of the carbon dioxide exhaled and the oxygen consumed and represent, more strictly speaking, the dry matter of body substance burned.

Time does not permit further analysis of our experiments. Some of the most important factors affecting the losses from the skin and from the lungs are, naturally, the volume of inspired air, its humidity and temperature and, above all, the temperature of the expired air. When the apparatus is weighed on the balance, it is impracticable to measure the volume of the inspired air, but if the bathing-cap expansion chamber is replaced by a spirometer placed on a table nearby, which connects through a large calcium chloride tube with the air circuit, the movements of the spirometer bell as registered on a kymograph give an accurate measure of the volume of air inspired. Finally, the measurement of the temperature of the expired air has been made possible by use of a thermo-junction system connected with a very good Einthoven string galvanometer. We are, therefore, able to photograph simultaneously the respiration curve and the temperature curve of the entire respiratory cycle. With these data we believe that a more careful analysis of the factors influencing respiration as well as the insensible loss may be made.

Although the results are in large part for one special subject, with whom experiments without clothing could be made, at least a dozen other persons have been studied with ordinary clothing, and the general deduction can be made that the total insensible loss in weight of the average woman, resting quietly, will be about 20 or 30 grams per hour. That of the average man will be nearer 40 grams per hour. Of this about 45 per cent is in water from the skin, about 45 per cent is in water from the lungs, and 10 per cent represents the difference between the intake of oxygen and the output of carbon dioxide. The effects of the removal of clothing,

of wind movement and of temperature below the point when visible perspiration occurs are astonishingly small, chiefly because the skin temperature is profoundly lowered by such measures. The total insensible loss is a reliable index of the total metabolism and is finding use in modern clinics.

HERMAPHRODITISM IN A DIOICOUS HEPATIC

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Communicated May 14, 1927

There are in botanical literature several reported cases of hermaphroditism in species of hepatics generally recognized as dioicous. In none, however, of these cases of which I am aware does all possibility of error seem to be entirely excluded. Hermaphroditic individuals, if found in species regularly dioicous, would seem to offer opportunities for critical tests of some of the current chromosomal and factorial hypotheses of six inheritance.

One hermaphroditic plant (now a small clone in two parts) of *Pellia Neesiana* Limpr. has been under observation since April, 1926, although its bisexual character was not recognized until several months later. The status of this species is still questioned by some hepaticologists who regard it as a sub-species of *P. epiphylla* Corda, which latter is regularly monoicous or bisexual. My observations of thousands of individual plants of *P. Neesiana* in California, Germany and Switzerland convince me that it is, though somewhat variable, distinct from *P. epiphylla* and that it is strictly dioicous—the one bisexual individual, for cogent reasons, not constituting a valid objection to this definition of the species.

Plants of this species were collected April 2, 1926, on the northward slope of the Wieswaldkopf about three kilometers from Posthalde (Baden), Germany. They were dormant, some had recently been exposed by the melting of the snow, and others were taken from the snow; all were discolored—slight traces of chlorophyll being apparent only in the younger portions of the thalli. Of the larger thalli, a few bore sporophytes and a considerable number had archegonial involucres in which could be found vestiges of old archegonia. Most of the smaller thalli bore no recognizable sex-distinguishing characters, but some of them were probably male.

At another station several hundred meters distant, where there was no snow and where there is at all seasons of the year much less water, were found male thalli in much better state of preservation. These also were still dormant but had retained their chlorophyll. They were uniformly smaller than female thalli and bore numerous antheridia in various stages

of development, showing that they had continued to be sexually active until the end of the preceding season of growth.

Thalli recognizable as female, by the presence of archegonial involucres, were planted in a series of cultures at the Botanical Garden of the University of Freiburg (Germany). Included among these was one large thallus bearing an unmistakable archegonial involucre and showing in its dorsal surface a series of pits strikingly similar to those (on male thalli) in which are borne antheridia. These pits were attributed to the biting of insects, or other small Arthropoda, which had bitten and torn many of the thalli in less methodical ways. Male thalli were planted in a separate culture.

These cultures were cared for by one of the gardeners and were observed at intervals by Prof. F. Rawitscher, to both of whom I am sincerely grateful.

Upon my return to Freiburg four months later these cultures were found to contain each a compact cushion of thalli with many mature sex organs. In one of the cultures of females were found about a dozen large vigorous thalli bearing many antheridia. These were pulled out and discarded as presumable males which had been included among the females by errors of identification.

A careful examination of the female thalli with which the supposed males had been in immediate contact showed only a single thallus bearing evidence of fertilization. This thallus bore a young sporophyte (probably about three weeks old) and, in a portion of its dorsal surface, unmistakable antheridial pits. A freshly torn posterior margin showed that it had been continuous with some, at least, of the thalli discarded as males. This thallus, thus recognized as hermaphroditic, was removed to a new culture. The original culture, cleaned of supposed male thalli, was inseminated with antherozoids from typical male thalli and provided many cases of fertilization, as did also other female cultures in which no male thalli had appeared, and which were similarly inseminated. It seems probable, therefore, that the thalli discarded as males and the thallus bearing the young sporophyte and antheridial pits were vegetative branches of a single bisexual individual—presumably the original thallus with its unmistakable archegonial involucre and the supposed methodically distributed insect wounds. It seems probable also that antherozoids from this bisexual individual are unable to fertilize eggs of typical female thalli.

The isolated bisexual thallus grew vigorously, the new branches bearing antheridia, and its sporophyte, though maturing late, attained a size well above the average of typical sporophytes of this species. On October 26th, two short lateral branches, each with a dozen or more partially developed antheridia, were removed and planted in a new culture. This was transported, starting November 1st, with other cultures of typical plants to Cornell University where it and they have been subsequently under close observation.

In my cultures of this species both at Freiburg and at Cornell the female thalli are appreciably larger than are males. The difference in width is especially noticeable, females exceeding males by 60 to 80 per cent. The males have slightly more distinct midribs and bear antheridia during the whole year. Female thalli with developing sporophytes were vegetatively dormant during autumn and early winter, but those with no sporophytes and those from which the sporogones were removed grew and proliferated freely but produced no sexual organs until late in March. Sporophytes in the cultures transferred to Cornell matured in late January and early February—the "spores" being multicellular when discharged, as in *P. epiphylla* and *P. Fabbroniana*. (The mother thalli had been inseminated August 14th, at Freiburg.) Thalli which had borne sporophytes became vegetatively active immediately after the "spores" were discharged.

The hermaphroditic thallus was wide like typical females during the summer and early autumn, though at no time was it observed to be without antheridia. The portions formed (at Cornell) during the late autumn and winter were narrow like typical male thalli (but thicker) and bore more antheridia per unit area of dorsal surface than did typical males, but produced no archegonia. Early in March the growing ends of the thalli widened out abruptly and the production of antheridia was greatly reduced; on some of the branches it ceased altogether. A little later, and simultaneously with the first appearance of archegonia on typical female thalli, archegonia appeared on several branches of the hermaphroditic clone. On one branch a group of archegonia is enclosed in an involucre as on typical female thalli, but on other branches the archegonia are distributed singly over the median portion of the dorsal surface in a manner similar to the usual distribution of antheridia. Some of these latter appear to be aberrant in form and may possibly be intersexual gametangia.

The portion of the bisexual thallus with the sporophyte was left at Freiburg until March 26th, when it was carried in person to Antwerp by Dr. Lenette M. Rogers and from Antwerp to New York by Dr. R. Cordier, both of whom are herewith tendered my heartiest thanks. This culture, and those transferred in November, were kept in cold storage during the ocean passage. Upon its arrival in New York the sporophyte was found to be mature, as was also a second very small sporophyte which Prof. Rawitscher had previously reported by letter to have appeared in the same involucre. When unpacked and exposed to the air both capsules dehisced, the large one yielding many "spores" and the small one only a few. The "spores" appeared to be normal and were sowed (April 13th) on sterilized clay. The early stages of germination have been passed successfully and many sporelings are now readily visible under the hand lens.

This large sporophyte required approximately three months longer to reach maturity than did sporophytes on typical female plants insemi-

nated in August and transferred in November to Cornell. This difference may be due, wholly or in part, to differences of conditions in the greenhouse at Freiburg as compared to the corresponding conditions at Cornell, but I have no data on which to base a comparison of these conditions.

The hermaphroditic clone is still too small to furnish ample material for exhaustive cytological studies, but a preliminary examination shows that it is almost unquestionably diploid, a condition not previously recorded in the Hepaticae—excluding the Anthocerotae. (The haploid number of chromosomes in this species is nine).

It is very desirable that bryologists study carefully any cases of apparent or suspected hermaphroditism in supposedly dioicous species of hepatics and report their results.

Note. While this paper was in press there appeared a paper by Lorbeer (*Zs. Ind. Abst. Vererb.*, **34**, 1–109) in which he describes in this species and in *P. Fabbroniana* a hitherto unknown situation with regard to the sex-chromosomes. I have convincing, though as yet not quite conclusive, evidence of an *xy* pair of sex-chromosomes similar to those of *Sphaerocarpos* except that the difference in size is not so striking. In the gametophytic mitoses of the typical plants one chromosome (presumably the sex-chromosome) shows a tendency to remain condensed during the telophases and to some extent throughout the interphases.

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MODIFICATIONS OF NERVE CENTERS DUE TO THE TRANSPLANTATION OF THE EYE AND OLFACTORY ORGAN IN ANURAN EMBRYOS

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We used, for the transplantation, embryos of *Rana temporaria* and *Bufo vulgaris* at the tail bud stage. The grafts were homioplastic. We excised the otic vesicle of the host and transplanted, according to the series of operations: 1. The optic vesicle and the corresponding lens placode alone. 2. These tissues and the olfactory organ placode. 3. The eye and olfactory organ placodes and a portion of the telencephalon adjacent to the olfactory organ of variable size. We studied the transplanted organs from the day of the operation up to a very advanced stage, after metamorphosis, and studied particularly the nervous relations of the transplanted organs, using the method of transplantation of organs as a source of information on the more general questions of neurotropism and neurobiotaxis.

The transplanted eyes and olfactory organs develop synchronously with

these organs in the host. Thus the formation of a lens optic, nerve, visual cells, and retinal layers of the grafted eye takes place at the same time as the formation of these parts in the normal eyes of the host. This synchronicity of development is apparently the result of an external factor, perhaps hormone-like in nature. The grafted organs persist after metamorphosis.

There is a marked affinity, during the first stages of development, between the optic neuroblasts and those of the central nervous system. While this fact falls in line with the theory of neurobiotaxis of Kappers, it may be distinguished from it as being its simplest expression. We have called this phenomenon *neuroblastotropism*.

The optic nerve, both in normal and in transplanted eyes, makes its appearance six days after the operation. The optic nerve of the transplanted eye, already at the first stages of its formation and connection with a cranial ganglion, determines a hyperplasia of the latter. Thus, in a case where an optic nerve of a transplanted eye, the first day of its formation, penetrated into a Gasserian ganglion, it determined a ganglionic hyperplasia of 22.51%.

The nerve of a transplanted sensory organ that merely goes through a cranial ganglion causes no hyperplasia of this ganglion. But when it penetrates into a cranial ganglion (Gasserian, glossopharyngeal-vagus complex) it determines a hyperplasia which varies from 28.4 to 78.9%. The connection of a transplanted eye with the acustico-facial ganglion across the macula acustica of an ear which was not excised also determines a ganglionic hyperplasia (24.2%).

Where merely a few axons penetrate into a cranial ganglion the resulting hyperplasia is small (13.7%). Thus the hyperplasia of a ganglion due to its connection with a sensory organ by means of the latter's nerve is a function of the number of fibers which penetrate into the ganglion.

The force of attraction exercised by a nerve center on a sensory organ may deform the latter. One sees transplanted eyes, connected with the Gasserian ganglion or the macula acustica of an ear which had not been excised, which are deformed at the place where this connection occurs.

A piece of telencephalon, grafted along with the sense organs, retains its anatomical individuality. One sees in many cases ventricles in such transplanted pieces of telencephalon. Such fragments of telencephalon attract, in many cases, the optic nerve of transplanted eyes. They also attract, in some cases, the cells of cranial ganglia (Gasserian, acusticofacial). In the cases where a piece of grafted telencephalon becomes fused with the medulla, these two parts of the central nervous system retain their normal architecture.

It appears that it is the absence of a pia-mater which allows the neurotactic substances or currents to diffuse and thus to bring about a close connection between the optic nerve of a transplanted eye and the grafted

telencephalon. The pia-mater must constitute a barrier which is crossed with difficulty by incoming axons, and it is probably because of its presence that direct connections between transplanted eyes and olfactory organs, on one hand, and the medulla, on the other, are so rare. A grafted telencephalon, without a pia-mater, is easily penetrated by the axons; a cranial ganglion, surrounded by a thin capsule, offers more resistance to its penetration, but this may occur without too much difficulty; while a medulla, surrounded by a developing cranium, a dura-mater and a pia-mater, is reached only rarely by the developing axons.

There are, however, cases in which the optic and olfactory nerves of transplanted organs enter into the medulla. The penetration of an embryonic optic nerve into the medulla determines a migratory avalanche of the medullar cells about it. The connection of the nerve of a grafted olfactory organ with the medulla determines in it a hyperplasia (4.26%) and a cellular migration toward the entering nerve. The medullar hyperplasia, like that of the cranial ganglia, appears to be in direct relation, as to its magnitude, with the number of penetrating axons. When the medullar hyperplasia is very large (24.61% excess of grey matter on the hyperplastic side) it reflects back on the medullar cells and fibers caudally to the connection.

The excision of the embryonic eye and olfactor organ usually causes no morphological change in the central nervous system. In some cases, however, the diencephalon and telencephalon react by neoformations. These neoformations are growths of the nervous substance which alter the normal form and are supplementary to it. They are totally different from the hyperplasias due to connections with the sensory organs.

Our results are added proof for the theory of neurotropism of Ramón y Cajal and the theory of neurobiotaxis of Kappers. We give them in detail, and discuss them at length in the "Archives de Biologie," fasc. 3, 1927.

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*ON THE GROWTH, CARE AND BEHAVIOR OF LOGGERHEAD TURTLES IN CAPTIVITY**

BY SAMUEL F. HILDEBRAND AND CHARLES HATSEL

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Prof. G. H. Parker (1926, p. 422) contributed some interesting information on the rate of growth of the loggerhead turtle, *Caretta caretta*, showing that growth in at least some individuals is more rapid than it is supposed to be according to current, or popular, opinion. The rate of growth of two loggerhead turtles held in captivity at the Fisheries Biological

Station at Beaufort, N. C., for six years, although not as rapid as Professor Parker reports for turtles from southern Florida, nevertheless was reasonably fast.

On July 11, 1912, Mr. W. P. Hay of the Washington, D. C., Public Schools found a nest containing 135 eggs on the sea beach of Bogue Banks. The nest had been made only a few hours previously, as shown by the fresh tracks of the female that had layed the eggs which had not been obliterated below the high water line by the tide.

Mr. Hay removed the eggs from the nest; the upper surface of each egg, as it lay in the nest, was marked with a soft lead-pencil and placed in a bucket in the same position for transfer to the station. The eggs, with as little handling as possible, were buried near the laboratory in what appeared to be suitable places, by scooping beds in the sand to a depth of about 10 or 12 inches. The eggs were placed in the holes, one on top of another, being careful to keep the pencil marks up, and the holes then were refilled with sand, making a cover of about 6 inches for the upper eggs. One lot of 35 eggs was placed where the sand was covered with water several times during high tides. These eggs rotted. The other lot of 100, buried where the "nest" was not flooded, fared better, as all except 10 eggs hatched. Five of these eggs were infertile, and three embryos had died within the shell. The incubation period was 64 days.

The young at hatching appeared to have disproportionately long anterior flippers. The plastron and the carapace, respectively, had a length of about 30 and 42 millimeters. These young creatures appeared to be unable to descend to the bottom of the aquarium in which they were kept and remained constantly at the surface. Feeding was not successful until the food (fish) was suspended at the surface of the water. Even after the animals had learned to feed and had gained some growth, they still seemed to be unable to submerge to any extent and the suspension of the food at the surface was continued.

Many of the young loggerheads died from time to time. Quite a number of them died of heat when the glass aquarium with glass cover, in which they were held, one day became exposed to the sun. Another lot died from cold early in the winter of 1912 in an outside pound to which they had been transferred earlier in the season. Finally, when only a few individuals were left, the animals were transferred to the terrapin nursery house, maintained at the station, where they were kept warm.

It is evident that loggerhead turtles are quite sensitive to the cold and upon the approach of cool weather they appear to leave, at least, the shallower waters of the vicinity of Beaufort, N. C. It was shown by confining (in 1916) three wild turtles, weighing from 40 to 60 pounds in an inclosure, containing about two feet of water at low tide and about five feet at high tide, that even larger animals will not survive the winter in

shallow water, as two of these turtles apparently were frozen to death on December 14, 1916, when the minimum temperature of the air reached 26 degrees F. and the other one succumbed on February 3, 1917, when the temperature of the air dropped to 13 degrees F. These animals, unlike the diamond-back terrapins did not bury in the mud or crawl under grass or other objects for protection but were rather active until killed by the cold.

Only two individuals of the lot of loggerhead turtles hatched during the summer of 1912 survived the first winter. These animals for six years were kept in the hot house each winter and in one of the outside terrapin pounds during the summer. They were fed principally on fish, although blue crabs occasionally were furnished. When they had attained an age of about three years and a considerable size, hard clams in the shell occasionally were provided, which they were able to crush with the greatest ease.

During the first year or two the young loggerheads were gentle but at about three years of age they began to fight each other and would strike at the hand of a person, if held somewhere near reach. They continued to become more vicious as they grew larger and older. The last two winters, when they were held in a rather deep wooden tank in the terrapin house, they fought almost continuously, though without injuring each other seriously, and frequently they splashed most of the water out of the tank in the process. Finally at the age of six years they had become so large and quarrelsome that sufficient space no longer could be provided in the hot house and the animals were liberated. At first they did not appear to want to leave and they swam along the shores of the Island upon which the Fisheries Laboratory is situated for a half hour or so. Then they disappeared and were seen no more.

A record of the rate of growth of these two animals was made, for they were measured or weighed, or both, at least once a year. However, some of these data appear to have been misplaced, and only the following are now available.

The length of the plastron at hatching was 3.0 centimeters, and that of the carapace 4.2 centimeters. The length of the plastron of one of the animals at one year of age was 10.6 centimeters, and that of the carapace 13.6 centimeters. The length of the plastron of the same animal at $4^1/_2$ years of age was 42.15, and the carapace 53.8 centimeters. This turtle, when the last mentioned measurements were taken, that is, at $4^1/_2$ years of age, weighed 45 pounds and the other one weighed 47 pounds. When liberated at the age of approximately 6 years they weighed, respectively, 55 and 61 pounds.

These animals appear to have been a little smaller at hatching than the ones from southern Florida reported upon by Parker (1926, p. 423), and their rate of growth somewhat slower. The reason or reasons for the retarded growth are not evident, although the longer and colder winters at Baufort, notwithstanding the fact that the animals were kept in a hot

house, may have checked the growth. Certainly the very close quarters in which the turtles were confined during the winter were objectionable. Then there was the lack of outdoor air, and probably other adverse conditions. Or again, it is possible that the two turtles simply were slower growing animals than the Florida turtles. Parker (1926, p. 423) has called attention to the great difference among individuals in the rate of growth of cold-blooded animals, including diamond-back terrapins. The present authors have shown (1926, p. 13) that some individuals among lots of diamond-back terrapins, kept under identical conditions, require two and even three times as long to reach sexual maturity, and a marketable size, as others. The reason for such great fluctuations are still unknown. A uniform rate of growth, as a matter of fact, cannot be said to take place among individuals in domestic animals that have been subject to selective breeding for many years, and the presence of slow growing animals continues to be a drawback to the stock breeder. It seems reasonable, therefore, to expect large fluctuations in the rate of growth among animals that have seldom, if ever before, been grown in captivity and which have not been subject to selective breeding beyond nature's selection, namely the "survival of the fittest."

* Published by the permission of the Commissioner of Fisheries.

Parker, G. H., "The Growth of Turtles," *Proc. Nat. Acad. Sci.*, **1926**, pp. 422–423, Washington.

Hildebrand, Samuel F., and Hatsel, Charles, "Diamond-Back Terrapin Culture at Beaufort, N. C.," *U. S. Bureau of Fisheries Economic Circular*, No. **60**, 1926, 20 pages, 8 figures, Washington.

MAGNETIC HYDROGEN ATOMS AND NON-MAGNETIC MOLECULES

By William Albert Noyes

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Read before the Academy April 26, 1927

Ten years ago it was suggested[1] that an electron rotating about two positive nuclei might hold atoms together. In 1923, Sidgwick[2] and Knorr,[3] quite independently of each other and of the other paper, proposed the same hypothesis in a much better form. More recently Pauling[4] and Grimm and Sommerfeld[5] have supported the same view and Glockler[6] has given some experimental basis for it in the relation between the ionization potentials of methane and argon.

Recently, Phipps and Taylor,[7] by very ingenious further development of the methods of Gerlach and Stern[8] and of Kunz, Taylor and Rodebush[9] have demonstrated the magnetic character of isolated hydrogen atoms.

Hydrogen molecules are non-magnetic and Lewis[10] has pointed out

that atoms with an even number of electrons are usually non-magnetic.

The magnetic character of hydrogen atoms suggests the following pictures of hydrogen atoms and molecules and of helium atoms, as possible:

Isolated hydrogen atoms might orient themselves, loosely in pairs with the rotation of their electrons in the same direction, but they would be prevented from combining by the repulsion between the nuclei and also that between the electrons.

Under the catalytic effect of a metal (Langmuir's hydrogen blowpipe) the orbits of the electrons may be assumed to take opposite directions, with the two nuclei between the planes of the two orbits. There would be a magnetic repulsion between the orbits but the electrons would be held to their orbital positions by their attraction for the nuclei and would fall closer to these because there are now two nuclei instead of one. This would account for the large dissipation of energy when two hydrogen atoms unite to form a molecule.

It seems possible that helium atoms may be formed in a somewhat analogous manner. Two hydrogen molecules would come together with the four nuclei between the planes of two electrons, which would fall very close in, while the two other electrons would assume orbits at a greater distance. Since the mass of a helium atom is eight-tenths of one per cent less than that of four hydrogen atoms, the energy evolved in such a process would be of a wholly different order from that involved in the formation of a hydrogen molecule.

Some mathematicians, physicists and physical chemists are suspicious of mechanical models or pictures. I am well aware that the suggestion here presented has only a very problematical value. It can be permanently useful only in case some one can find a method of subjecting it to a rigid mathematical analysis and it should be found in accord with all the experimental facts by means of which it can be tested.

The successes which have followed Dalton's pictures of atoms and the pictures of the structure of molecules given us by Couper and Kekulé, give us some reason to hope that other pictures may be of service.

[1] Noyes, *J. Amer. Chem. Soc.*, **39**, 879 (1917). The fact of discrete helium nuclei in radio-active elements misled me to the supposition of four positive nuclei in a carbon atom and only single electrons were postulated. These parts of the suggestion were, doubtless, wrong.

[2] Sidgwick, *J. Chem. Soc.*, **123**, 469 (1923); *Trans. Faraday Soc.*, **19**, 109 (1923).

[3] C. A. Knorr, *Z. anorg. Chem.*, **129**, 109 (1923).

[4] Linus Pauling, *J. Amer. Chem. Soc.*, **48**, 1132 (1926).

[5] Grimm and Sommerfeld, *Z. Physik*, **36**, 52 (1926).

[6] Glockler, *J. Amer. Chem. Soc.*, **48**, 2021 (1926).

[7] Phipps and Taylor, *Science*, **64**, 480 (1926).

[8] Gerlach and Stern, *Z. Physik*, **9**, 349, 353 (1922).

[9] Kunz, Taylor and Rodebush, *Science*, **63**, 550 (1926).

[10] G. N. Lewis, "Valence and the Structure of Atoms and Molecules," p. 148 (1923).

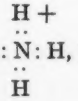
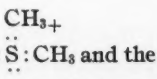
THE RELATION OF THE OCTET OF ELECTRONS TO IONIZATION

BY WILLIAM ALBERT NOYES

CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS

Read before the Academy April 27, 1927

The theory of the electronic structure of atoms, proposed by G. N. Lewis, supposes that there is a strong tendency for atoms to complete an outer shell of eight electrons by giving up or taking up one or more valence electrons to form ions or by sharing pairs of electrons to form "non-polar" unions. In this manner the atom of an ion assumes the structure of an atom of one of the noble gases but with the difference that in the ion the positive charge of the nucleus is either greater or less than the number of electrons in the shell by a whole number of units. For example, the electronic structures of the sodium ion, neon, the chloride ion and argon are supposed to be:

In complex ions, such as the ammonium ion,  , the sulfonium ion  , and the hydroxide ion, , there is, also, always some central atom which has completed its octet but the group contains too few or too many electrons to balance the positive charges of the nuclei of the atoms present.

These relations and the effect of the dielectric constant of the solvent have been recognized but the physical significance of the completed octet does not seem to have been so clearly seen.

Atoms of the noble gases do not combine with each other or with the atoms of other elements because the exact balance between their nuclear charges and the charges of their electrons prevents them from sharing electrons with other atoms. In the normal gaseous state, isolated atoms and molecules of all kinds are electrically neutral and exert no electrical attraction or repulsion toward each other, while at some distance. When they approach closely, however, the electrons forming their external shells must exert a strong repulsion, causing them to separate. This furnishes a very simple explanation for the elastic collisions postulated in the kinetic theory. The fact that electrons can gain or lose energy only in "quanta"

may explain why such collisions do not permanently distort the orbits of the electrons.

We may suppose that we have very similar phenomena when the ions having a noble gas structure approach each other in a solution. In spite of the static attractions between ions of opposite sign, their external shells of electrons will cause so great a repulsion on close approach that they will separate and maintain their independent existence after collision. This gives to solutions of ions their close analogies to the properties of a gas. These properties are also dependent on the dielectric medium but that side of the picture need not be discussed here.

It is well known that compounds of hydrogen are ionized to a much smaller degree than the corresponding compounds of the alkali metals. This is, doubtless, because the hydrogen ion has no external electron and, hence, may approach much closer to a negative ion, or may, perhaps, be included within the orbits of a pair of electrons belonging to the negative ion.

ULTRA-VIOLET SOLAR RADIATION

By Edison Pettit

Mount Wilson Observatory, Carnegie Institution of Washington, Pasadena

Communicated May 14, 1927

The work of Abbot and his colleagues[1] has shown that the radiation from the sun varies and that the variation is most pronounced in the violet end of the spectrum. Whether we regard the variation as due to a change in temperature, a variable transmission of the outer solar envelope or a variable emissivity, this effect on the ultra-violet is to be expected. Dobson in England,[2] using a photographic method, measured the ultra-violet solar radiation transmitted by silver films on 34 days in 1922, and found variations as great as 500 per cent and a standard daily range of 30 per cent outside the atmosphere. It occurred to the writer that the uncertainties of photography could be eliminated by measuring the radiation directly with a thermocouple; that disturbances of the atmosphere could be made differential by standardizing the ultra-violet with the green region of the spectrum, which varies only slightly; that the accuracy could be increased by making the apparatus automatic, which would permit an increase in the number of observations; and that the combination of this procedure with the favorable atmospheric conditions on Mount Wilson might lead to results of some interest.

This was accomplished by an apparatus constructed as follows. In

figure 1, A is a spindle carrying a disk, D, having two cells set diametrically opposite one another. Cell S contains a quartz lens and plate, both silvered chemically on their inner surfaces with two coats of silver. Cell G contains a similar quartz lens and plate, both coated on the inner surfaces with gold by sputtering. These are crossed lenses, giving minimum spherical aberration, and are of one inch aperture and two inches focal length. The separators are formed to fit the surfaces, producing practically air-tight contacts. Diaphragms in contact with the plates are used to adjust the galvanometer deflections in the apparatus on Mount Wilson, but not in the Tucson apparatus, about to be described. Exposed to the sun, the lens forms an image of it, $^1/_2$ mm. in diameter, in ultra-violet light of wave-length 0.32μ, on one junction of the compensated thermocouple, C. An

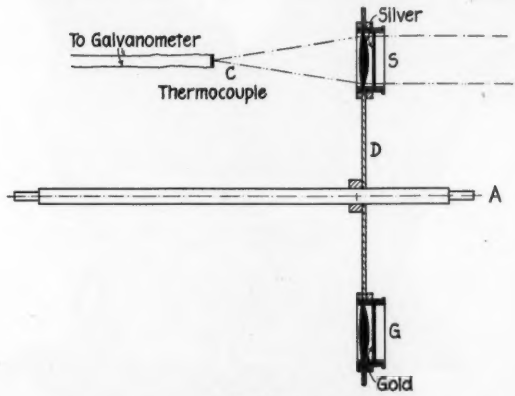


FIGURE 1
Diagram of optical system of ultra-violet solar radiometer.

escapement attached to the spindle A, operated electrically by a contact clock, causes the image to fall first on one, then on the other junction of the compensated thermocouple, then permits the disk to rotate a half revolution, and repeats the process, substituting the gilded lens which transmits green radiation in wave-length 0.50μ. The deflections thus produced in the galvanometer attached to the thermocouple by the ultra-violet and green radiations from the sun are recorded photographically on a moving plate and determine the ratio, ultra-violet to green radiation, every four minutes.

Plate I shows a radiometer recently installed at the Desert Sanatorium of Southern Arizona at Tucson. In this instrument the thermocouple is in an air-cell having a large heat capacity, and not in a vacuum as on Mount Wilson. This makes it possible to compare the galvanometer deflections themselves, since the sensitivity is constant there being no

secular change due to state of vacuum. The motor, M, working through a friction disk, exerts a continuous torque on the spindle which is permitted to rotate only at intervals of one minute when the escapement E

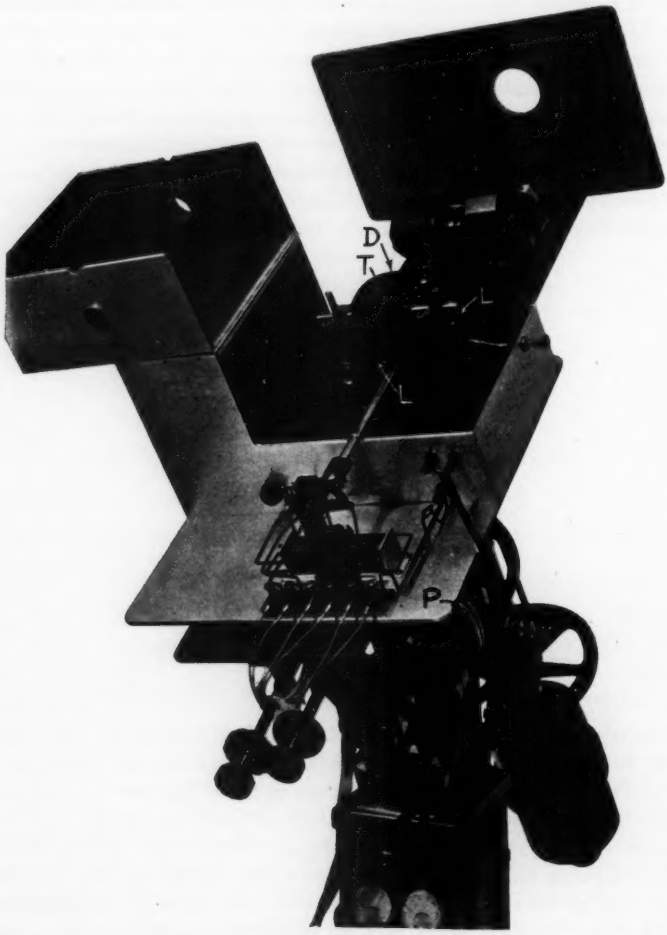
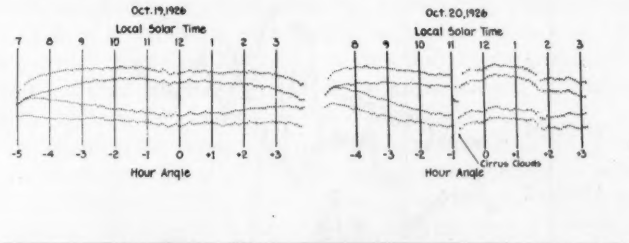


PLATE I
Ultra-violet solar radiometer at Tucson.

is released by the magnets. An air cell thermocouple, T, having quartz windows and receivers 1 mm. square is connected to a D'Arsonval galvanometer in the room below. D is the disk carrying the lenses L. A wire running over a pulley P on the polar axis has the moving plate attached

to the other end upon which are registered photographically the deflections of the galvanometer.

Figure 2, upper part, shows reproductions of the galvanometer records for October 19 and 20, 1926. The inside rows of dots are produced in each case by the radiation transmitted by silver, $\lambda = 0.32\mu$, while the outside


Oct. 19, 1926
Local Solar Time
7 8 9 10 11 12 1 2 3
-5 -4 -3 -2 -1 0 +1 +2 +3
Hour Angle
Oct. 20, 1926
Local Solar Time
8 9 10 11 12 1 2 3
-4 -3 -2 -1 0 +1 +2 +3
Cirrus Clouds
Hour Angle

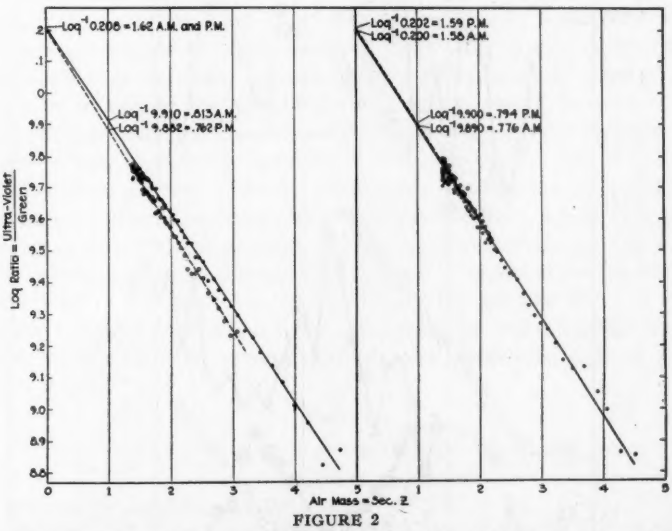

Log⁻¹ 0.208 = 1.62 A.M. and P.M.
Log⁻¹ 9.910 = .813 A.M.
Log⁻¹ 9.882 = .762 P.M.
Log⁻¹ 0.202 = 1.59 P.M.
Log⁻¹ 0.200 = 1.58 A.M.
Log⁻¹ 9.900 = .794 P.M.
Log⁻¹ 9.890 = .776 A.M.
Log Ratio = Ultra-Violet / Green
Air Mass = Sec. Z

FIGURE 2

Radiometer records and plots for October 19 and 20, 1926, illustrating at left a typical day with afternoon run affected by haze, and, at right, a day with no haze in the afternoon.

rows are due to the radiation transmitted by gold, $\lambda 0.50\mu$. The heavy lines are hour-angle marks, put on by the contact clock, and indicate local solar time. It will be seen that the ultra-violet light is zero for some time after sunrise, reaching a maximum at noon, whereas the green radiation has a sensible value at sunrise and rapidly approaches its maximum. The lower part of figure 2 shows a graphical solution for each of the plates. The logarithm of the ratio, ultra-violet to green radiation, is plotted against

secant Z obtained from the hour-angle. This plot is a straight line from which two values are taken, that for the zenith, sec $Z = 1$, and that for no atmosphere.

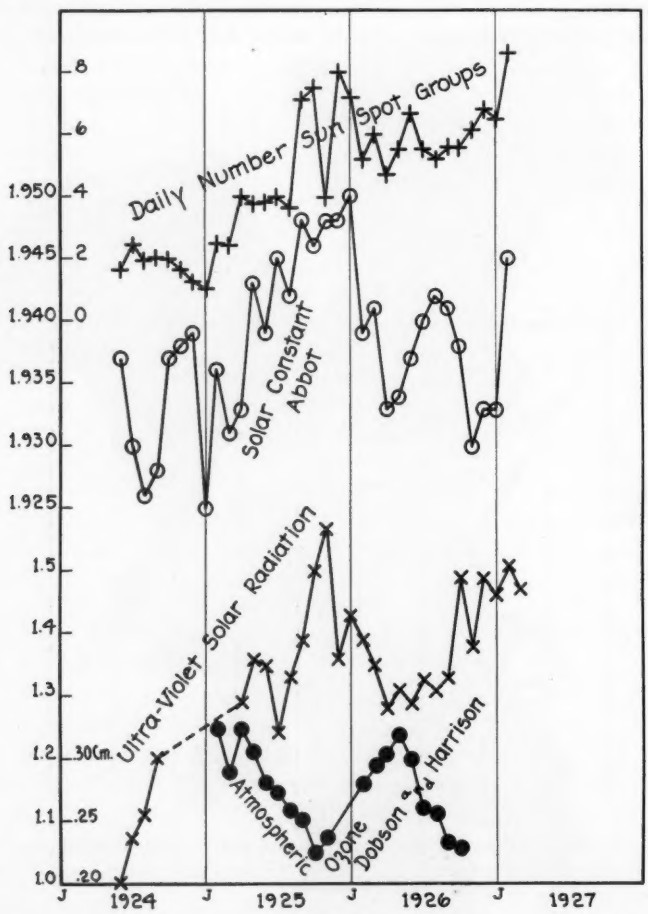


FIGURE 3

March of the monthly means of atmospheric ozone, ultra-violet solar radiation, solar constant, and sun-spot group numbers.

Figure 3 shows the march of the monthly means of the ratio, ultra-violet to green, since May, 1924, compared with Dobson's and Harrison's measurements of ozone (below), Abbot's measurements of the solar constant, and the Mount Wilson daily sun-spot group numbers (above).

Considerable correspondence will be noted in the general trend of the last three curves. The ultra-violet values are for no atmosphere, but practically the same curve would result if the values for one atmosphere were used, so nearly are the atmospheric disturbances eliminated.

The ozone curve seems to run counter to the ultra-violet curve. The ozone curve represents a seasonal variation, although it is difficult to see how the obvious explanation of changing solar declination can apply, since the time of maximum ozone lags behind the time of maximum insolation, rather than the contrary, which we might expect. Probably it is too early to draw conclusions in this connection.

That variations in the ozone content of the atmosphere do not sensibly affect these measurements of ultra-violet radiation was shown by placing a tube of ozone in the optical path of the instrument and varying the pressure in the tube. In this way it was shown that an increase of 100 per cent in ozone decreases the ultra-violet measurements only 5 per cent, while complete elimination of ozone increases them only 3 per cent. That transmissions of the filters are not affected by exposure to sunlight was shown by increasing the area of the diaphragms placed in front of the lenses, thus exposing previously unexposed portions of the filters after the apparatus had been in operation more than two years. The deflections increased in proportion to the increased area. In January of the present year the cells were taken apart and examined. No trace of tarnish or other defect was observed in the films. A careful determination of the transmission of both plates was made, and this will be repeated toward the end of the year to check further the stability of the metallic films.

Table 1 shows a comparison between the observed and computed atmospheric transmissions for several elevations for ultra-violet light of wavelength 0.32μ.

TABLE 1

			$E/E_0 = e^{-kH}$ COMP.			
	H (CM.)	E/E_0 OBS.	RAYLEIGH	CABANNES DUFAY	AIR MASS $= B/B_0$	LOG E/E_0 OBS.
Mt. Whitney (Smithsonian)	350,000	0.615	0.592	0.569	0.653	9.7889
Mt. Wilson	174,200	0.480	0.519	0.489	0.812	9.6812
Tucson	76,000	0.370	0.479	0.452	0.916	9.5682
Pasadena	25,800	0.325	0.466	0.440	0.969	9.5199
Oxford (Dobson)	6,400	0.315	0.452	0.427	0.993	9.4983
Sea Level	0	....	0.448	0.422	1.000	.....

$$k = \frac{32\pi^3(u-1)^2}{3N\ \lambda^4}\ \text{(Rayleigh)} = \frac{8\pi^3(u^2-1)^2}{3N\ \lambda^4}\frac{(6+3\rho)}{(6-7\rho)}\ \text{(Cabannes and Dufay)}$$

A very considerable disparity is noted as sea-level is approached. This is shown graphically in figure 4. Here the straight lines are the theoretical vertical transmissions computed from Rayleigh's law of scattering and the modified formula of Cabannes and Dufay[3] which takes polarization into

account. It will be noted that for air masses less than 0.8 (which is equivalent to an altitude of 6000 ft.) the transmission is greater than that called for by the theory, and at lower altitudes it is much less, being only 0.70 as great near sea-level. A direct comparison between Pasadena and Mount Wilson gave 65 per cent on a fairly clear day, which is in fair agreement with the value 69 per cent obtained from the transmission in table 1.

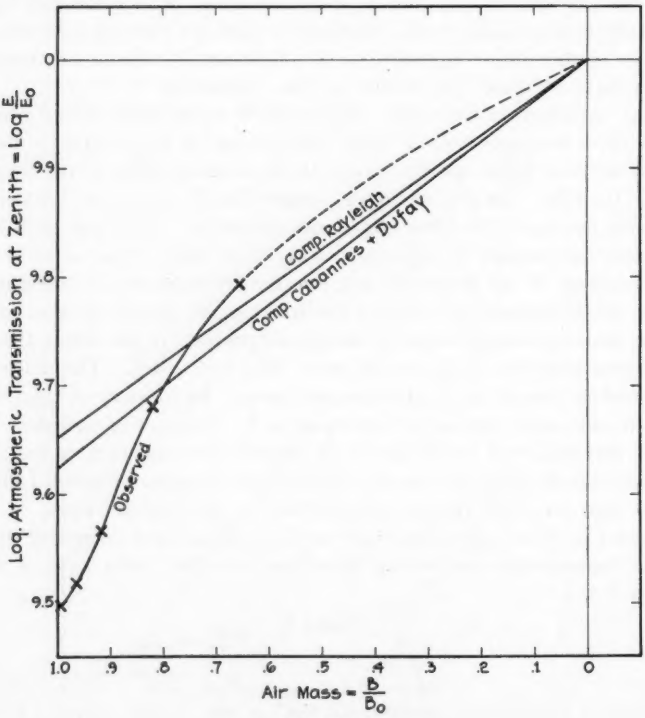


FIGURE 4

Comparison of the observed and computed atmospheric transmissions for ultra-violet light, $\lambda = 0.32\mu$.

Measurements of sky radiation effective on a horizontal surface determined photographically in wave-length 0.32μ show, for air mass 1.3, one-twentieth that of direct sunlight on Mount Wilson, and one-fourth that of direct sunlight in Pasadena on a fairly clear day. Under these conditions the radiation in this wave-length, falling on a horizontal plane surface from the sun and sky combined in Pasadena is 0.8 that on Mount Wilson, the greater radiation from the sky making up for the deficiency from direct sunlight to some extent.

A peculiar meteorological phenomenon has been noticed both in the Mount Wilson and Tucson measurements. When the sky is perfectly clear, so that no whiteness can be seen up to the limb of the sun from sunrise to sunset, the morning and afternoon observations agree in giving nearly the same results, i.e., the intensity of the ultra-violet light is the same for a given hour-angle east and west of the meridian. Ordinary clouds and haze do not seem to affect the ratio ultra-violet to green remarkably, but haze of another kind does. Estimates of the radius of the corona about the sun due to sky whiteness are made at intervals during each day's run and are recorded on a scale of 0 to 10. Generally, this whiteness is nearly zero until 11 A.M., then it begins to rise rapidly, attaining a value of 6 or 7 by 1 P.M., after which it gradually increases to 8 or 9 by sunset. This haze has the appearance of smoke, and in the afternoon may be seen from Mount Wilson, filling the valley below and rising in clouds considerably above the mountain. Figure 2 illustrates, at the right, a nearly perfect day, and, at the left, a typical day affected by haze in the afternoon. On account of this effect, only morning observations have been used to study the solar variation. It is possible that this phenomenon is connected with atmospheric ionization, and the afternoon runs may furnish material for its study.

[1] *Ann. Astroph. Obs., Smithsonian Institution,* **4**, 206, 1922.
[2] *Proc. Roy. Soc.,* **104**, 252, 1923.
[3] *J. Physique Radium,* **7**, 257, 1926.

ON THE DISTANCE OF THE SUN FROM THE GALACTIC PLANE

BY B. P. GERASIMOVIČ AND W. J. LUYTEN

HARVARD COLLEGE OBSERVATORY

Communicated April 27, 1927

It is a well-known fact that when a plane of symmetry is determined from the positions on the sphere of various classes of galactic objects the intersection of this plane with the celestial sphere is not a great circle, showing that the sun is not situated in this plane of symmetry but is displaced to the north of it. From the observed angular "dip" of the circle of symmetry of stars of given apparent magnitude, the elevation of the sun above the galactic plane may be calculated when the absolute brightness of the stars under consideration is known, and conversely, once the linear distance of the sun to the galactic plane is known, the angular "dip" of a group of stars may be used to estimate their absolute brightness.

The existing determinations of the elevation of the sun above the galactic

plane (E) are very discordant, ranging from 0 (Seares[1]) to 250 parsecs (Kreiken[2]). These discordances may be easily explained by the method used; using the faint stars of the galactic regions we are dealing with very large distances and a small uncertainty of the curves of equal density leads to very large variation in E which measures the eccentric position of the sun inside these curves. On the other hand, using the different objects which show galactic concentration we get concordant values of E.

It seems, therefore, that at present the most reliable values of E are those calculated by means of objects showing strong galactic concentration—stars of Classes O and B, the c and ac stars, and the Cepheid variables. Of these stars we have recent determinations of E for all, except the Cepheids.

Cepheids.—Hertzsprung[3] in 1913 derived a value of +37 parsecs for E using 68 Cepheids; in 1918 with a different selection and weighting of the material Shapley[4] derived $E = +60$. Considering the large number of Cepheids discovered in recent years a new determination of E which also makes use of a more accurately determined period luminosity curve may be of value. For this purpose we have taken all stars in Abteilung II of the Astronomische Gesellschaft Catalogue of Variable Stars[5] for 1927 with periods between one and forty days, which are known to be Cepheids. Using the recently determined photographic period luminosity curve[6] and adopting the A. G. data on the spectra to establish the color indices of variables observed visually, the following preliminary four values of E (arithmetic means in parsecs) were calculated.

$E = +42$ using only stars which at minimum are brighter than 8.5 (vis.) or 9.0 (pg.) (45 stars)
$E = +38$ using stars brighter than 9.0 (vis.) 9.5 (pg.) (54 stars)
$E = +39$ using stars brighter than 9.5 (vis.) 10.0 (pg.) (78 stars)
$E = +34$ using stars brighter than 10.0 (vis.) 10.5 (pg.) (100 stars)

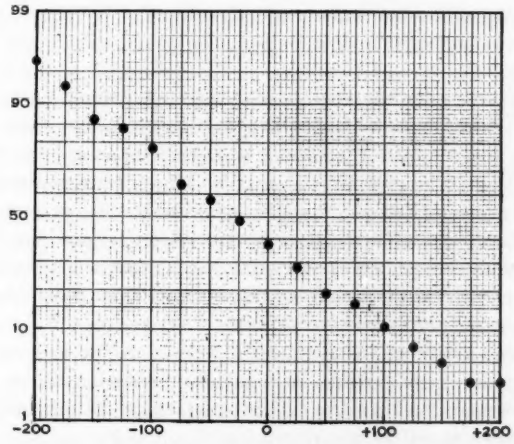
The good agreement between these values indicates that the mean value of E may be considered as statistically stable and not dependent upon selection in apparent magnitude, at least for magnitudes brighter than 10.5. The Cepheids fainter than this limit are mostly confined to restricted regions in the sky, especially near η Carinae, in Cygnus, Aquila and Cassiopeia. Inclusion of these stars would make the whole material statistically inhomogeneous on the one hand and would tend on the other hand to make the resulting value of E dependent upon the average galactic latitude of one or two particular regions. It seems therefore that restriction to stars brighter than apparent magnitude 10.5 in minimum (photographic) is justifiable inasmuch as it will give us a material of optimum homogeneity.

The distribution of the Z coördinates of 100 Cepheids is shown in figure 1

plotted on probability paper. The ordinates represent the number of stars whose Z coördinates are algebraically larger than the values indicated by the corresponding abcissae. We read from the curve

$$\text{Mean } Z = -32, \qquad \text{Probable error} = 70$$

(strictly speaking these are the median and the quartile deviation). The computed arithmetic mean is -35, closely agreeing with the value found here from the integrated curve. We may, therefore, adopt as a final value



for the elevation of the sun above the plane defined by the Cepheid variables:

$$E = +34 \pm 11 \text{ (mean error)}$$

c and ac Stars.—Using only the three clusters of *c* stars in Carina, Scutum, and Perseus and adopting -3.2 as mean absolute magnitude of these stars, Schilt[7] has derived a value of $+53$ parsecs for the distance of the sun from the galactic plane. It seems to us that a more generally representative value of E may be derived by using the angular dip of $-1°.0$ found by Schilt from all the *c* and *ac* stars (400 in number). Retaining his value of -3.2 for the mean absolute magnitude we then find:

$$E = +33$$

O and B Stars.—Gerasimovič has derived a value of $+31 \pm 6$ parsecs using 144 non-Magellanic *O* stars.[8] Using all *B*0 and *B*5 stars of the H. D. C. between 6.7 and 8.75 apparent magnitude the same investigator[9] found $E = +34$ parsecs with an estimated mean error of not more than 4 parsecs. This value was derived not from the apparent elevation but by calculating the coördinates of the center of gravity.

We thus have:

Cepheids	$E = +34$ parsecs
c and ac stars	$E = +33$ parsecs
O stars	$E = +31$ parsecs
B stars	$E = +34$ parsecs.

The four different determinations lead to such closely accordant results that it seems unnecessary to consider the matter of giving different weights to the individual values and we adopt

$$E = +33 \text{ parsecs}$$

as the best value for the elevation of the sun above the galactic plane defined by the Cepheid variables, the O, B and c and ac stars. The mean error of this result is estimated at not more than 3 parsecs.

Novae.—It may be of interest to apply the results derived above to the problem of novae. For two reasons, however, it does not seem advisable to do so at present; firstly, because the observational data are largely subject to selection on the basis of apparent magnitude, and secondly, since some novae are known to have originated from dwarf stars, it is not *a priori* evident that novae must have a strong galactic concentration. The combined effect of these causes is visible in the lack of correlation between apparent magnitude and galactic latitude. If novae have a galactic concentration then the existing material is statistically incomplete and the results would be too dependent upon single cases (e.g., Nova T Coronae and Nova Aquarii).

M-Supergiants.—In their recent paper on the parallaxes of M stars Adams, Joy and Humason[10] make the statement that the M giants with absolute magnitude brighter than -1.0 show a pronounced galactic concentration. It is rather unfortunate that the number of stars available is too small to afford an independent accurate determination of E. Rejecting the stars in the h and χ Persei cluster there remain only 20 stars, for which the Mount Wilson parallaxes give a mean Z coördinate of $+18 \pm 9$, or $E = -18$, thus placing the sun on the south side of the plane of these M stars.

[1] Seares, *Amer. Astr. Soc.*, Dec., **1926.**
[2] Kreiken, *M. N. R. A. S.*, **86,** 1926 (665).
[3] Hertzsprung, *A. N.*, **196,** 1913 (207).
[4] Shapley, *Mt. Wilson Contr.*, **157,** 1918 (23).
[5] *Kleinere Veroff. Babelsberg*, **1,** 1927.
[6] Shapley, Yamamoto, and Wilson, *Harv. Circ.*, **280, 1925.**
[7] Schilt, *B. A. N.*, **48,** 1924 (47).
[8] Gerasimovič, *A. N.*, **226,** 1926 (327).
[9] Gerasimovič, *V. J. S., A. G.*, **61,** 1926 (227).
[10] Adams, Joy and Humason, *Ap. J.*, **64,** 1926 (225).

THE RELATIONSHIP OF SPECTRAL TYPE TO PERIOD AMONG VARIABLE STARS

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Although it is well known that among the variable stars of the Cepheid class the spectral type is, in general, more advanced the longer the period of light variation, the faintness of many of the stars has prevented the derivation of any definite correlation between these two important quantities. Such a relationship, however, is vital in considerations of the luminosity of these stars and their connection with other types of variables.

We have recently devoted considerable time with the 100-inch telescope to the observation of the radial velocities and spectral types of Cepheid variables, extending our results to stars of about the tenth magnitude visually. Sixty-four stars have been included, the observations in the majority of cases covering the maximum and minimum of light and some intermediate phases. In addition to the Cepheids we have secured spectrograms during past years of 27 short-period cluster-type variables which in the form of their light-curves resemble the Cepheids closely. There is, however, a marked interval between the longest period of the cluster-type variables and the shortest period of the Cepheids within which no stars are known, and this gap separates the two classes definitely.

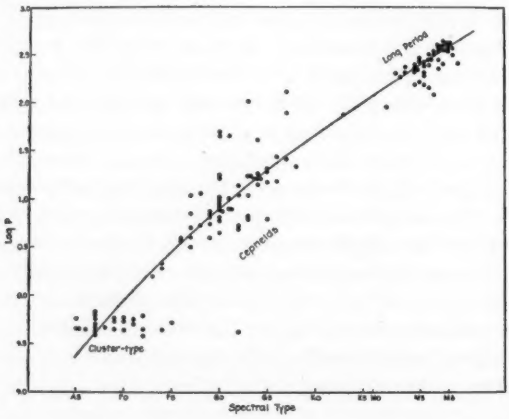
The spectral types of these stars have been determined by the aid of standard spectra selected from among the stars themselves. These have been chosen after a careful study of the spectral criteria of the successive types of the Harvard system and are as follows:

SHORT-PERIOD VARIABLES	PHASE		CEPHEID VARIABLES	PHASE	
VX Herculis	Max.	A3	RT Aurigae	Max.	cF5
Z Can. Ven.	Max.	A5	RS Orionis	Max.	cF8
RX Eridani	Max.	F0	SV Persei	Max.	cG0
RS Boötis	Max.	F2	TT Aquilae	Min.	cG4
SW Androm.	Min.	F5	RS Puppis	Min.	cG6
			S Vulpeculae	Max.	cK0
			V Vulpeculae	Min.	cK2

All of the spectrograms of the stars were compared with these standard spectra under a Hartmann spectrocomparator and estimates were made in the case of intermediate values. Since the variation of spectral type with phase of light is well known, the results in the case of each star were reduced to a median value by applying a positive correction of two units to the spectral type at maximum of light and a negative correction of the same amount at minimum. The final result for each star is the mean of

all these reduced values. This simple method has the advantage of being based on a uniform system and is especially suitable when a differential comparison is desired.

The relationship of spectral type to period for these stars proved of sufficient interest to suggest the possibility of the inclusion in the investigation of the other principal type of variable stars, the long-period red variables. A list of 44 of these stars was selected from among those observed by Dr. Merrill, and determinations of spectral type were made from standard spectra, Merrill's values and our own being assigned equal weight. The observations of these stars were all near maximum of light; and, since little is known regarding the spectrum of most of them at other phases, the spectral types have been used without correction. Their periods range between 90 and 444 days.



The spectral types of the individual stars are shown in figure 1 plotted against the logarithms of their periods of light variation. The principal features are the rather surprising way in which the majority of the stars fall on a smooth curve not very different from a straight line, and, on the other hand, the outstanding deviations of many of the short-period variables and of a few of the Cepheids. The short-period stars whose periods, with but few exceptions, group closely about 0.5 day show a considerable range in spectral type. Among the Cepheids there is a small group with the longest periods of any stars of this class, all of which have spectral types considerably less advanced than would be expected from the behavior of the majority. One of these stars, SX Herculis, has bright hydrogen lines, and Luyten's observations have indicated the presence of bands near minimum. The spectra of at least two of the others are somewhat peculiar. The periods of these stars all fall above the gap between 27

and 42 days (within which few Cepheids are known at present), tend toward irregularity and in some cases are none too certain. It is possible that these stars form a separate group, perhaps related to the irregular *M*-type variables.

The brightest and best known Cepheids show a correlation between spectral type and logarithm of period which is practically linear within the errors of observation. That the long-period variables and the mean values for the short-period cluster-type variables should be so nearly represented by the curve for the Cepheids is an unexpected feature of the results, and one which is probably significant in the interpretation of the relationship of these different classes.

HIGH-DISPERSION STELLAR SPECTRA AND SOME RESULTS OF A STUDY OF γ CYGNI

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One of the chief advantages of the coudé form of mounting as applied to a large telescope is the opportunity it affords for the use of much more powerful spectroscopic apparatus than could be employed if it were attached to a moving instrument. The original design of the 100-inch reflector at Mount Wilson provided for a spectrograph of large size to be mounted on a pier in an enclosed room south of the telescope, the light passing into the room through the hollow polar axis. Last year a spectrograph of 15 feet focal length and 6 inches aperture was completed and installed, and a considerable number of photographs of the spectra of bright state has been obtained during the past few months. The spectrograph is of the auto-collimating type with a dense flint-glass prism of 53° angle through which the light is returned by a mirror. Two 10-inch plates of different photographic emulsions are used regularly in the plateholder, one for the blue, and the other for the green, yellow and red portions of the spectrum. The focal curve of the lens is such that with a suitable inclination of each plate within the holder good definition is obtained throughout the range from λ 4100 to λ 6700.

The linear scale of these spectrograms, about 2.9 angstroms to the millimeter at Hγ, is the largest ever used for stellar spectra, if exception is made of photographs of two or three of the brightest stars observed at Mount Wilson and elsewhere some years ago. The resolving power and definition are such that these spectra are especially suitable for studies of the intensity and identification of lines, and the long range of spectrum

covered makes it possible to examine the behavior of different classes of lines to excellent advantage.

The spectra of the Cepheid variables and of stars of similar physical characteristics are of exceptional interest when studied on such a large scale, and we have given special attention to γ Cygni which has a spectrum nearly identical with that of some of the brighter Cepheids. The apparent magnitude of this star is 2.3, and exposure times of 3 hours have given excellent spectra 20 inches long, which are well measurable from λ 4120 to λ 6700. As is well known, its spectrum, which is usually classified as cG0, is characterized by great intensity of the lines of ionized elements, especially iron, titanium, chromium, and a few others. With the aid of these large-scale spectra we have also been able to measure and identify over 125 lines due to ionized cerium, lanthanum, scandium, yttrium and zirconium.[1] The presence of cerium and lanthanum suggested a search for lines due to the other rare earths and very definite evidence was found for the presence of neodymium and samarium. The following prominent lines of the arc spectra of these elements to the violet of λ 4500 have been measured in the spectrum of γ Cygni. Several other lines of longer wave-length have been identified, especially in the spectrum of samarium. It is probable that they belong to the ionized element, but this is as yet uncertain. The wave-lengths are on the international system, and only isolated lines in the spectrum of the star are included.

Nd	Sun	γ Cygni	Sa	Sun	γ Cygni
4135.33	.30	.35	4181.13	.08	.09
4232.39	.39	.40	4256.41	.42	.34
4284.50	.54	.52	4262.68	.71	.68
4314.50	.51	.53	4280.79	.79	.81
4338.73	.70	.72	4318.95	.94	.98
4358.21	.17	.14	4329.03	.05	.01
4385.71	.68	.66	4334.16	.19	.11
4446.42	.40	.37	4421.15	.13	.13
			4424.36	.37	.33
			4434.34	.34	.34
			4452.74	.74	.72
			4467.36	.34	.36

The evidence for the presence of the other rare earths, praesodymium, europium and gadolinium, although not so strong, is still fairly convincing. Miss Payne of the Harvard College Observatory has already called attention to the probable occurrence of two europium lines in the spectrum of γ Cygni.[2] Our measures confirm this conclusion, but indicate that the wave-lengths of the solar spectrum lines to be identified with europium differ from those given by Miss Payne. The following brief summary contains a list of the lines other than blends which have been ascribed to these elements.

Pr	Sun	γ Cygni	Eu	Sun	γ Cygni
4141.26	...	.20	4129.72	.73	.72
4143.13	.16	.16	4205.03	.03	.06
4222.99	...	.95		.08 V+	
4297.76	.75	.79			
4408.84	.80	.86			
5220.11	.09	.04	Gd	Sun	γ Cygni
			4130.44	.45	.42
			4251.75	.75	.72
			4342.19	.19	.13

The identification of the lines of these rare earths in the spectrum of γ Cygni recalls the identification of many lines of the same elements by Mitchell in the flash spectrum at the 1905 eclipse of the sun.[3] In many other respects the similarity of the stellar spectrum to that of the flash is so great that the spectrum of γ Cygni might, with a considerable degree of accuracy, be defined as a reversal of the spectrum of the solar chromosphere.

The study of the displacements of the lines of the different elements and of the lines of the normal and ionized atom in the case of the same element is an interesting and extensive field of investigation for which these large-scale spectra are especially well adapted. A series of measurements completed on spectrograms of γ Cygni affords good confirmation of the results obtained previously from a study of the spectra of a few of the brightest stars,[4] indicating a displacement toward the red of the enhanced lines with reference to the arc lines. The average difference measured as radial velocity between 26 enhanced lines, principally of iron, titanium and chromium, and 30 arc lines in 6 spectrograms of γ Cygni is

$$\text{Enhanced} - \text{arc lines} = +0.65 \text{ km./sec.}$$

A new and interesting result obtained from the measures is the marked systematic displacement found in the case of the Ce^+ lines. A list of 10 Ce^+ lines, selected as being, so far as possible, free from the influence of other elements, shows the following residuals for the 6 spectrograms when compared with the mean values given by a list of 30 arc lines, principally of iron.

Plate	Ce^+ − Arc
Coudé 18	−1.29 km./sec.
27	−1.74
32	−0.71
36	−1.49
38	−2.05
52	−1.45
	−1.45 km./sec.

A few lines due to La^+ give similar results, although the weight of the determination is much lower than in the case of Ce^+. It seems fairly

probable that this excess of negative velocity on the part of the lines of these elements of high atomic weight is to be ascribed to relative upward motion of the gases at the low levels at which they occur in the stellar atmosphere. These results accordingly may be interpreted as affording further evidence for the presence of convection currents such as have been inferred from solar and stellar observations by St. John and Babcock[5] and St. John and Adams.[6]

[1] Adams and Joy, *Pub. Astron. Soc. Pacific*, October, **1926.**
[2] Cecilia H. Payne, *Harvard College Observatory Bulletin*, 841.
[3] S. A. Mitchell, *Astrophys. J.*, **38**, 407, 1913.
[4] *Mt. Wilson Contr.*, No. 50; *Astrophys. J.*, **33**, 64, 1911.
[5] *Mt. Wilson Contr.*, No. 278; *Astrophys. J.*, **60**, 32, 1924.
[6] *Mt. Wilson Contr.*, No. 279; *Astrophys. J.*, **60**, 43, 1924.

GROUPS OF COLLINEATIONS IN A SPACE OF PATHS

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1. In a paper by Professor L. P. Eisenhart and the present writer entitled[1] "Displacements in a Geometry of Paths" we have obtained the equations that the components of an infinitesimal transformation must satisfy in order to carry the paths of an affine manifold into paths. We called such transformations *infinitesimal displacements* because from one point of view they are generalizations of *motion* in Riemannian geometry. However, Professor Eisenhart has pointed out that these transformations should be called *collineations*, since he has shown that for a projectively flat space, referred to a suitable coördinate system, these transformations are collineations. We shall, therefore, adopt this name for any space of paths. If the transformation is such that the affine parameter of the paths is preserved, it will be called an *affine collineation*, otherwise a *projective collineation*.

In the present note we shall obtain the conditions under which an affine manifold admits an r-parameter finite continuous group of collineations, stating the results and indicating the methods in the barest outline, leaving the formal proofs to a subsequent publication.

2. Since all projectively related manifolds admit the same projective collineations we choose one[2] for which the generalized Ricci tensor R_{ij} is symmetric and, therefore, the alternating contracted curvature tensor $S_{ij} = 0$. The equations of condition then become

$$\xi^i_{,j,k} - \xi^l B^i_{jkl} = \delta^i_j \varphi_{,k} + \delta^i_k \varphi_{,j}, \tag{2.1}$$

where

$$\varphi_{,j} = \frac{1}{n+1} \xi^h_{,h,j}.$$

The conditions of integrability of (2.1) are:

$$\xi^h B^i_{jkl,h} - \xi^i_{,h} B^h_{jkl} + \xi^h_{,j} B^i_{hkl} + \xi^h_{,k} B^i_{jhl} + \xi^h_{,l} B^i_{jkh} = \delta^i_l \varphi_{,j,k} - \delta^i_k \varphi_{,j,l}. \tag{2.2}$$

When these are contracted for i and l, we find

$$\varphi_{,j,k} = \frac{1}{n-1} (\xi^h R_{jk,h} + \xi^h_{,j} R_{kh} + \xi^h_{,k} R_{jh}), \tag{2.3}$$

so that (2.2) takes the form

$$\xi^h W^i_{jkl,h} - \xi^i_{,h} W^h_{jkl} + \xi^h_{,j} W^i_{hkl} + \xi^h_{,k} W^i_{jhl} + \xi^h_{,l} W^i_{jkh} = 0, \tag{2.4}$$

where W^i_{jkl} is the Weyl projective curvature tensor. The necessary and sufficient condition that (2.1) should form a completely integrable system, is that (2.4) be satisfied identically; this is equivalent to $W^i_{jkl} = 0$. In case $n \neq 2$, the vanishing of the Weyl tensor also makes (2.3) completely integrable. If $n = 2$, $W^i_{jkl} \equiv 0$ but the complete integrability of (2.3) depends upon the vanishing of the projective covariant.[3] Therefore, for all values of n (2.1) will be completely integrable only if the space is projectively flat.

If $W^i_{jkl} \neq 0$, we build sets of equations for the algebraic determination of the unknown quantities ξ^i, $\xi^i_{,j}$ and $\varphi_{,j}$. Calling these sets $F^{(1)}$, $F^{(2)}$ . . . , we may write them in the form

$$F^{(\alpha)}; \quad \xi^i D^{(\alpha)}_i + \xi^i_{,j} C^{(\alpha)j}_i + \varphi_{,j} E^{(\alpha)j} = 0 \quad (\alpha = 1, 2, \ldots), \tag{2.5}$$

where $D^{(\alpha)}$, $C^{(\alpha)}$ and $E^{(\alpha)}$ are tensors depending upon B^i_{jkl}, W^i_{jkl} and their covariant derivatives of orders not higher than α.

Professor O. Veblen and Dr. J. M. Thomas[4] have established a general existence theorem for systems of partial differential equations of the first order. For the particular problem under discussion this may be expressed in the form:

The necessary and sufficient condition that (2.1) admits a solution, is that a positive integer N (≥ 1) exist, such that the rank of the matrices of $F^{(1)}$ . . . , $F^{(N)}$ and of $F^{(1)}$ . . . , $F^{(N+1)}$ be the same.

If the condition of the theorem is satisfied and the rank of the matrices is $n^2 + 2n - r$, the general solution of (2.1) will depend on r arbitrary parameters. Assuming this to be the case and letting $\xi^i_{(\alpha)}$ ($\alpha = 1, \ldots, r$) be the r independent solutions of (2.1), any other must be of the form $a^\alpha \xi^i_{(\alpha)}$, where the a's are arbitrary constants.

If $\xi^i_{(\alpha\beta)}$ are the components corresponding to the alternant of two generators, (X_α, X_β), they satisfy (2.1) in virtue of (2.4) and of the fact that

$$\xi^h_{(\alpha\beta),h,j} = (\xi^k_{(\alpha)}\varphi_{(\beta),k})_{,j} - (\xi^k_{(\beta)}\varphi_{(\alpha),k})_{,j}.$$

This fact, coupled with the first theorem in our previous paper, gives the theorem:

If (2.1) admits r independent solutions, the manifold admits an r-parameter finite continuous group of projective collineations.

The greatest number of parameters possible in a group of projective collineations is $n^2 + 2n$ and only projectively flat spaces admit such a group. In this case, if the coördinates are cartesian, the coefficients of projective connection are zero and (2.1) reduce to

$$\frac{\partial^2\xi^h}{\partial x^i \partial xj} = \frac{1}{n+1}\left(\delta^h_i \frac{\partial^2\xi^k}{\partial x^k \partial xj} + \delta^h_j \frac{\partial^2\xi^k}{\partial x^k \partial x^i}\right), \tag{2.6}$$

the solution of which gives

$$\xi^i = x^i a_j x^j + b^i_j x^j + c^i \tag{2.7}$$

the finite transformations generated being of the form

$$x^i = \frac{A^i_j x^j + B^i}{1 + C_k x^k}$$

which is the result to which we referred in §1.

3. The problem of affine collineations is solved by considering the equations

$$\xi^i_{,j,k} = \xi^l B^i_{jkl}. \tag{3.1}$$

The necessary and sufficient condition that these be completely integrable, is the vanishing of the curvature tensor B^i_{jkl}. If this is not the case we build sets of equations analogous to (2.5)

$$F^{(\alpha)}; \quad \xi^i G^{(\alpha)}_i + \xi^i_{,j} H^{(\alpha)j} = 0 \quad (\alpha = 1, 2, \ldots), \tag{3.2}$$

where $G^{(\alpha)}$ and $H^{(\alpha)}$ are tensors depending on B^i_{jkl} and its covariant derivatives of orders not higher than α. If the rank of the matrices of $F^{(1)}, \ldots, F^{(N)}$ and of $F^{(1)}, \ldots, F^{(N+1)}$ is $n^2 + n - r$, the manifold will admit an r-parameter finite continuous group of affine collineations.

Only flat spaces admit a group of affine collineations of the greatest number of parameters, $n^2 + n$. For this case, the coördinates being cartesian, the coefficient of affine connection are zero and (3.1) become

$$\frac{\partial^2\xi^i}{\partial xj \partial x^k} = 0$$

the solution being

$$\xi^i = a^i_j x + b^i,$$

the finite transformations generated being of the form

$$\bar{x}^i = A^i_j x^j + B^i. \tag{3.3}$$

It can be easily shown that two motions in a Riemann space cannot have the same path-curves.[5] Two collineations may have the same path-curve. In the case of projective collineations the solutions of (2.1) must satisfy additional conditions of the form

$$\xi^i_{,j} = \psi_j \xi^i + \delta^i_j f \tag{3.4}$$

where the vector ψ_j is given by a set of partial differential equations and the scalar f is obtained by contraction.

In case of affine collineations the solutions of (3.1) must satisfy

$$\xi^i_{,j} = \psi_j \xi^i. \tag{3.5}$$

Since in either case the vector ξ^i determines a congruence of paths, we have the theorem:

If a space admits two collineations having the same path-curves, these path-curves must be paths.

4. Another question of importance is whether there exists an affine manifold admitting a given simply transitive group of collineations. This leads to a generalization of Bianchi's theorem for Riemannian geometry and our method is generalized from that used by Professor Eisenhart in establishing Bianchi's theorem.[6]

If $\xi^i_{(\alpha)} (\alpha = 1, \ldots, n)$, $\left|\xi^i_{(\alpha)}\right| \neq 0$ are the n vectors of the group, we define the covariant vectors $\eta_i^{(\alpha)}$ by the equations

$$\xi^i_{(\alpha)} \eta_j^{(\alpha)} = \delta^i_j. \tag{4.1}$$

The quantities

$$R^h_{ij} = -\eta_j^{(\alpha)} \frac{\partial \xi^h_{(\alpha)}}{\partial x^i} = \xi^h_{(\alpha)} \frac{\partial \eta_j^{(\alpha)}}{\partial x^i}$$

satisfy the relations

$$R^h_{ij} - R^h_{ji} = -c^\gamma_{\alpha\beta} \xi^h_{(\gamma)} \eta_i^{(\alpha)} \eta_j^{(\beta)}, \tag{4.2}$$

$c^\gamma_{\alpha\beta}$ being the constants of composition of the group, and

$$\frac{\partial R^h_{jk}}{\partial x^l} - \frac{\partial R^h_{jl}}{\partial x^k} = R^h_{pk} R^p_{jl} - R^h_{pl} R^p_{jk}. \tag{4.3}$$

If a manifold is to exist admitting the given group as a group of projective collineations, the equations

$$\frac{\partial \Pi^h_{ij}}{\partial x^k} = \frac{\partial R^h_{ik}}{\partial xj} - R^h_{im} R^m_{jk} - \Pi^m_{ij} R^h_{mk} + \Pi^h_{im} R^m_{jk} + \Pi^h_{mj} R^m_{ik} + \frac{1}{n+1} \left\{ \delta^h_i \left(R^p_{pm} R^m_{jk} - \frac{\partial R^p_{pk}}{\partial xj} \right) + \delta^h_j \left(R^p_{pm} R^m_{ik} - \frac{\partial R^p_{pk}}{\partial x^i} \right) \right\} \tag{4.4}$$

must have a solution such that $\Pi^h_{ij} = \Pi^h_{ji}$, $\Pi^h_{ht} = 0$ and which will transform according to the law of transformation of the coefficients of projective connection. By repeated application of (4.2) and (4.3) we find that (4.4) are completely integrable and although in general the solutions will not be coefficients of projective connection, $\infty^{\frac{n(n-1)(n+2)}{2}}$ of them will satisfy all the conditions of the problem.

The same set of vectors $\xi^i_{(\alpha)}$ can serve as the components for a simply transitive group of affine collineations, as the equations

$$\frac{\partial \Gamma^h_{ij}}{\partial x^k} = \frac{\partial R^h_{ik}}{\partial xj} - R^h_{im}R^m_{jk} - \Gamma^m_{ij}R^h_{mk} + \Gamma^h_{im}R^m_{jk} + \Gamma^h_{mj}R^m_{ik} \qquad (4.5)$$

are also completely integrable. The general solutions of (4.5) are coefficients of *asymmetric connection*, $\infty^{\frac{n^2(n+1)}{2}}$ of them being coefficients of affine connection. There exists only one manifold, its coefficients of connection being R^i_{jk}, with respect to which each of the given vectors $\xi^i_{(\alpha)}$ is a parallel vector field.

[1] Eisenhart, L. P., and Knebelman, M. S., these PROCEEDINGS, **13**, 1927, p. 38.
[2] Eisenhart, L. P., *Ibid.*, **8**, 1922, p. 236.
[3] Veblen, O., and Thomas, J. M., *Ann. Math.*, **27**, 1926, p. 287.
[4] Loc. cit., pp. 288–291.
[5] Eisenhart, L. P., *Riemannian Geometry*, **1926**, Chap. VI.

REMARKS ON THE QUANTUM THEORY OF DIFFRACTION

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1. *On Fraunhofer Diffraction Phenomena.*—Before attacking the Fresnel problems we shall restate some of the considerations of our last paper, dealing with the Fraunhofer diffraction in a new form suitable for generalization.[2] The main question discussed in that paper was as to the intensity of light diffracted by any optical structure at a given angle to the incident beam. We saw there that the "electronic intensity," ρ of the diffracting system is a function of the space which may be referred to any system of coördinates. Let us use a rectangular cartesian system x, y, z and denote the cosines of the angles between the axes and the direction of the incident ray by α_0, β_0, γ_0.

The general expression for the electronic density can then be given in terms of a three-fold Fourier integral

$$\rho(x, y, z) = \int_{-\infty}^{+\infty} d\omega_1 \int_{-\infty}^{+\infty} d\omega_2 \int_{-\infty}^{+\infty} A_{\omega_1\omega_2\omega_3} \cos(\omega_1 x + \omega_2 y + \omega_3 z - \delta_{\omega_1\omega_2\omega_3}) d\omega_3, \quad (1)$$

where

$$A_{\omega_1\omega_2\omega_3} e^{i\delta_{\omega_1\omega_2\omega_3}} = \frac{1}{8\pi^3} \int_{-\infty}^{+\infty} du \int_{-\infty}^{+\infty} dv \int_{-\infty}^{+\infty} \rho(u, v, w) \cos(\omega_1 u + \omega_2 v + \omega_3 w) dw. \quad (2)$$

This means that the actual electronic density can be always built up by a superposition of a three-fold infinity of sinusoidal elementary lattices. Each elementary lattice consisting of uniform plane layers perpendicular to the direction $(\omega_1 x + \omega_2 y + \omega_3 z)/\sqrt{\omega_1^2 + \omega_2^2 + \omega_3^2}$.

On the other hand we have seen in section 3 of the paper referred to that, from a classical point of view, the mean amplitude of the secondary radiation emitted in a direction α, β, γ is the modulus of

$$S(\alpha, \beta, \gamma) = C \int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} dy \int_{-\infty}^{+\infty} \rho e^{i\frac{2\pi}{\lambda}[x(\alpha-\alpha_0)+y(\beta-\beta_0)+z(\gamma-\gamma_0)]} dz. \quad (3)$$

We see that the expressions of A and S become identical (apart from the constant C), when

$$\omega_1 = 2\pi(\alpha - \alpha_0)/\lambda, \quad \omega_2 = 2\pi(\beta - \beta_0)/\lambda, \quad \omega_3 = 2\pi(\gamma - \gamma_0)/\lambda. \quad (4)$$

This means that out of our infinity of lattices only that one is responsible for the reflected beam (3) for which the coefficients ω_1, ω_2, ω_3 satisfy relations (4). In fact, let us consider the special case when our structure is of such a constitution that A has a finite value only for the arguments (4) and is zero for all other values of ω_1, ω_2, ω_3. From the comparison of (2) and (3) it follows that the diffracted intensity will have a finite value only for the direction α, β, γ and will vanish for all other directions. The general case can be regarded as a superposition of such special cases, so that each elementary lattice throws its whole intensity in only one direction.

It is useful to adapt the system of coördinates to the direction of the diffracted ray under consideration. Let us consider the directions of the primary and the secondary ray as known and including an angle 2φ, and let us choose as x-axis the bisectrix of the angle between the secondary ray and the negative direction of the primary, as y-axis the bisectrix of the adjacent angle (between the positive directions of the primary and the secondary ray) and as z-axis the perpendicular to x and y. We will have then $\alpha = \cos\varphi$, $\alpha_0 = -\cos\varphi$, $\beta = \beta_0 = \sin\varphi$, $\gamma = \gamma_0 = 0$. Equations (4) take the form

$$\omega_1 = 4\pi \cos\varphi/\lambda, \qquad \omega_2 = 0, \quad \omega_3 = 0 \quad (5)$$

This means that the plane layers of the responsible lattice are at right angles to the x-axis and in a position with respect to the primary and secondary ray corresponding to a regular reflection from those layers. The spacing a of this lattice is connected with ω_1 by the relation $2\pi/a = \omega_1$ and satisfies, therefore, the Bragg relation

$$2a \cos \varphi = \lambda. \tag{6}$$

The expression (3) for the reflected intensity assumes the simpler form

$$S = C \int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} dy \int_{-\infty}^{+\infty} \rho e^{i\omega_1 x} dz. \tag{7}$$

It was shown in paper I (section 2) that in the act of reflection the x-component of the momentum carried by the light wave is changed by the amount h/a for every energy quantum $h\nu$.

2. *Fresnel Diffraction from the Classical Point of View.*—We shall use the same degree of accuracy that is used in most text books[3] developing the Huyghens principle. That is, we shall assume that the amplitude of the primary wave at a distance r from the source of light O is given by e^{ikr}/r. If this wave falls on a diffracting structure having the electronic density ρ, every element of this structure becomes a secondary source emitting light according to the same law. In a second point O' the intensity of the scattered or diffracted light is, therefore, represented by the modulus of the well-known expression

$$S = C \int\int\int \frac{e^{i\frac{2\pi}{\lambda}(r+r')}}{rr'} \rho dx\, dy\, dz \tag{8}$$

where r denotes the distance from O to the scattering element $dx\, dy\, dz$, r' the distance from that element to O', and where the integral is to be extended over the whole volume of the diffracting structure.

We can construct an analogy with formula (7) of the last section if we introduce instead of the cartesian coördinates x, y, z a new system of curvilinear variables, so that $r + r' = \xi$ is one of them. This can be done in the following way. Let us denote the distance OO' by f, let us choose the origin of the cartesian system in the middle of that distance, and the x-axis coinciding with the line OO'. The new coördinates ξ, η, φ will then be given by the relations

$$\begin{aligned} x &= \frac{1}{2f} \xi\eta, \quad y = \frac{1}{2f} \sqrt{\xi^2 - f^2} \cdot \sqrt{f^2 - \eta^2} \cos \varphi, \\ z &= \frac{1}{2f} \sqrt{\xi^2 - f^2} \cdot \sqrt{f^2 - \eta^2} \sin \varphi. \end{aligned} \tag{9}$$

The surfaces ξ = const. are a family of confocal stretched ellipsoids of rotation while the surfaces η = const. are the orthogonal family of confocal hyperboloids. We have further

$$\xi = r + r', \qquad \eta = r - r' \tag{10}$$

The line elements in the respective directions ξ, η, φ are given by

$$ds_\xi = \frac{1}{2}\sqrt{\frac{\xi^2 - \eta^2}{\xi^2 - f^2}}\, d\xi, \qquad ds_\eta = \frac{1}{2}\sqrt{\frac{\xi^2 - \eta^2}{f^2 - \eta^2}}\, d\eta,$$
$$ds_\varphi = \frac{1}{2f}\sqrt{\xi^2 - f^2}\cdot\sqrt{f^2 - \eta^2}\, d\varphi. \tag{11}$$

The volume element, correspondingly,

$$dV = \tau(\xi, \eta, \varphi) d\xi\, d\eta\, d\varphi = \frac{1}{8f}(\xi^2 - \eta^2) d\xi d\eta\, d\varphi. \tag{12}$$

Finally the angle ψ between r and the normal to the ellipsoid ξ = const.

$$\cos\psi = \sqrt{\frac{\xi^2 - f^2}{\xi^2 - \eta^2}}. \tag{13}$$

With these substitutions $\tau/rr' = 1/2f$, so that (8) becomes

$$S = \frac{C}{2f}\int_f^{+\infty} d\xi \int_{-f}^{+f} d\eta \int_0^{2\pi} \rho e^{i\frac{2\pi}{\lambda}\xi}\, d\varphi. \tag{14}$$

The analogy with the case of the last section is a far reaching one. As there by formula (1), we can represent ρ by a Fourier expression. The only difference is that, due to the finite variability of η (from $-f$ to $+f$) and φ (from 0 to 2π), two of the integrations must be replaced by summations:

$$\rho(\xi, \eta, \varphi) = \int_{-\infty}^{+\infty} d\omega_1 \sum_{-\infty}^{+\infty} n_2 \sum_{-\infty}^{+\infty} n_3 A_{\omega_1 n_2 n_3} \cos\left(\omega_1\xi + \frac{\pi}{f} n_2\eta + n_3\varphi - \delta_{\omega_1 n_2 n_3}\right) \tag{15}$$

$$A_{\omega_1 n_2 n_3} - e^{i\delta_{\omega_1 n_2 n_3}} = \frac{1}{8\pi^2 f}\int_{-\infty}^{+\infty} du \int_{-f}^{+f} dv \int_0^{2\pi} \rho(u,v,w,) e^{i(\omega_1 u + \frac{\pi}{f} n_2 v + n_3 w)}\, dw. \tag{16}$$

Again we see that the distribution of density can be represented by superposition of a three-fold infinity of curved elementary lattices. The comparison of (16) and (14) shows, in close analogy to section 1, that for the secondary pencil only that elementary lattice is responsible for which

$$\omega_1 = 2\pi/\lambda, \qquad n_2 = 0, \qquad n_3 = 0. \tag{17}$$

This means that the responsible lattice represents a sinusoidal succession of uniform layers characterized by the condition ξ = const. That is, the layers are ellipsoids of rotation having all the common focal line OO'. As the spacing of a lattice is given by the relation $\omega = 2\pi/a$ we see that in this case

$$a = \lambda. \tag{18}$$

From layer to layer the parameter ξ increases by a constant amount, equal to the wave-length. Such a lattice has the property of converting a divergent wave emitted in O into one converging toward O'.

3. *Momentum of the Primary and Secondary Waves.*—In this section we shall carry the analogy with the Fraunhofer case still farther and show that in the act of reflection from our ellipsoidal lattice there prevails a transformation of momentum quite similar to that discovered by Duane for the plane lattice. We shall call ξ-momentum the Lagrangean momentum conjugated with the variable ξ. The amount of ξ-momentum carried by the primary wave can be found in the following way. Let us consider an element $d\sigma$ of one of the ellipsoids ξ = const. and let us ask how much ξ-momentum dp_ξ passes through it in the short time dt, due to the primary wave motion. If this element of area suddenly became perfectly absorbing, it would absorb all of the radiation falling on it and acquire, in this way, the momentum dp_ξ in the time dt. As the momentum is the time integral of a force, we have

$$dp_\xi = f_\xi dt \tag{19}$$

if we denote by f_ξ the Lagrangean generalized force exercised by the primary wave on the absorbing element. If under the action of this force the element is displaced in the direction ξ so that the parameter ξ experiences an increase $d\xi$, the work of the force is given by

$$dW = f_\xi d\xi. \tag{20}$$

On the other hand, the same work in terms of the ordinary cartesian force F_ξ acting on the element in the normal direction, due to the light pressure, will be

$$dW = F_\xi ds_\xi. \tag{21}$$

Comparing the two expressions for dW we find $f_\xi = F_\xi ds_\xi/d\xi$ and

$$dp_\xi = F_\xi dt\, ds_\xi/d\xi. \tag{22}$$

The force F_ξ is known in theory of light pressure[4] to be $F_\xi dt = \cos\psi dE/c$, where dE denotes the energy falling on the area $d\sigma$ in the time dt and ψ the angle with the normal as in (13). It follows

$$dp_\xi = \frac{\cos\psi}{c}\frac{ds_\xi}{d\xi}\,dE. \tag{23}$$

Formulae (11) and (13) of section 2 show us that $\cos\psi\, ds_\xi/d\xi = {}^1/_2$, so that

$$dp_\xi = dE/2c. \tag{24}$$

As this relation is true for any pencil, it is true for any finite portion of the primary wave:

$$p_\xi = E/2c. \tag{25}$$

This is a portion of the primary wave having an energy E carries a ξ-momentum proportional to this energy, the constant of proportionality being $1/2c$.

Turning from the primary wave to the secondary, we notice that the conditions in the latter have a perfect symmetry with those in the former, the only difference being that the secondary wave is a convergent one so that the ξ-momentum has the opposite sign. We can, therefore, write

$$p'_\xi = -E/2c. \tag{26}$$

If the energy E, originally contained in the primary wave, by reflection from the elements of the grating, goes over to the convergent secondary wave, this act of reflection is connected with a change of ξ-momentum $p_\xi - p'_\xi = E/c$. In the special case, when we consider an amount of reflected energy $E = h\nu$, we have

$$\Delta p_\xi = h\nu/c = h/\lambda. \tag{27}$$

We have seen in section 2 that $\gamma = a$: the wave-length is equal to the spacing of the responsible lattice. The last relation, therefore, can be written

$$\Delta p_\xi \cdot a = h \tag{28}$$

in which form it shows a complete analogy with Duane's rule for the change of translatory momentum in the case of the Fraunhofer diffraction.

4. *Interpretation in Terms of Light Quanta.*—Let us regard the problem sketched in the beginning of section 2 from the point of view of light quanta. Light quanta of the frequency ν are emitted by the source O. They can be reflected in many different ways by the elements of the optical structure surrounding the source and having the electronic density distribution ρ. If, however, the analogy with the case discussed in section 1 holds still in the applications of the correspondence principle, we must expect that the probability of the light quanta being reflected into the point O' is associated with the same term in our Fourier expression (15)

which is responsible in the classical theory for converting the primary wave into a secondary wave converging towards O'. Speaking more definitely, the principles laid down in paper I let us expect that this probability will be proportional to the square of the amplitude $A_{\omega_1 n_2 n_3}$ of the responsible lattice, defined by the conditions (16) and (17).

The "mechanism" of this reflection can be described in the following way. Let us assume that our optical system is capable of a motion in which all the surfaces ξ = const. move in a normal direction so that each surface remains a confocal ellipsoid. The light quantum collisions of the above-considered type are such that they impart to our optical structure just such a motion. For the ξ-momentum Δp_ξ which the system can pick up in a collision with a light quantum we have to introduce the same quantum restriction as in the case of paper I

$$\int \Delta p_\xi d\xi = h$$

where the integral must be extended over a period of the corresponding lattice equal to $a = \lambda$, according to (18). We get again relation (28)

$$\Delta p_\xi \cdot a = h. \tag{28}$$

The mechanical meaning of the ξ-momentum possessed by our structure is the following. Let m be the mass density in any point of our structure, then the kinetic energy of a volume element dV in its motion in the ξ-direction will be

$$T = \frac{m}{2} (ds_\xi/dt)^2 dV = \frac{1}{2} m(ds_\xi/d\xi)^2 \dot{\xi}^2 dV.$$

The ξ-momentum of this element is, therefore, $\vartheta T/\vartheta \dot{\xi} = m(ds_\xi/d\xi)^2 \dot{\xi} dV$, while the total ξ-momentum becomes

$$p_\xi = \int m(ds_\xi/d\xi)^2 \dot{\xi} dV,$$

the integration being extended over the whole volume of the structure.

Since the momentum acquired by the diffracting structure is supplied by the light quantum, the latter loses an amount of ξ-momentum equal to $\Delta p_\xi = h/a = h/\lambda = h\nu/c$. As we have seen in section 2, the ordinary cartesian momentum M_ξ in the direction ξ is connected with the ξ-momentum by the relation $M_\xi ds_\xi/d\xi = p_\xi$, so that the light quantum undergoes in the collision a change of the ξ-component of its cartesian momentum which, on account of the relation $ds_\xi/d\xi \cos\psi = 1/2$, can be written

$$\Delta M_\xi = 2 \cos\psi \ \Delta p_\xi = 2h\nu \cos\psi/c. \tag{29}$$

The light quantum possesses a rectilinear momentum $h\nu/c$ in the direction of its motion. In the moment when it crosses a surface ξ = const. the normal component to this surface is $h\nu \cos\psi/c$, the tangential com-

ponent $h\nu \sin \psi/c$. Equation (29) shows us that in a collision the tangential component remains unchanged, while the normal loses the amount $2h\nu \cos \psi/c$ and becomes, therefore, $-h\nu \cos \psi/c$ or oppositely equal to its value before the collision. This change corresponds to a regular reflection from a surface ξ = const. and brings, therefore, the quantum to the second focus O' of the surface.

These considerations show us that if we had a structure just consisting of the elementary ellipsoidal lattice, all the light quanta going out of the focus O would be reflected into the focus O'. In section 2 we have seen that exactly the same conditions prevail in the case of light waves following the classical theory. If we have a more complicated structure, the principle of correspondence suggests that the probability of light quanta behaving in this way will be proportional to the square of the amplitude $A_{\omega_1 n_2 n_3}$ of the responsible lattice. On the other hand, according to formula (14), the intensity of the wave converging into O' will be expressed just by the same quantity $A^2_{\omega_1 n_2 n_3}$. It follows that the classical theory and the above-sketched adaptation of the quantum theory give identical results.

5. *Limitations of the Theory.*—At first sight it could seem that the agreement between the classical theory and the quantum theory is just as good in the case of Fresnel diffraction as in the case of Fraunhofer diffraction. A closer examination shows, however, that there is a considerable difference between the two cases. To account for the Fraunhofer phenomena we represent the electronic density as a superposition of elementary lattices which is *unique and independent of the incident and reflected radiation.* The different types of reflection we could interpret as collisions with the individual elementary lattices. On the other hand, describing the Fresnel phenomena, we adapted the Fourier integral (15) to the special positions of the source of light and the point of observation. The system of elementary lattices is no longer unique, and even if we keep the source of light in a constant position, we still have a different system for every point in which we observe the intensity. An attempt to solve this difficulty by attributing to all these systems equal probability and by postulating collisions with the constituent lattices of all of them fails for the following reasons. The number of these lattices is an infinity of higher order and, if only one of them should contribute to the reflection we are interested in, the intensity of this reflection must be infinitely small. On the other hand, through every point in our space there pass light quanta reflected to an infinity of other points and the question arises why they do not contribute to the intensity in the first point. It is, therefore, clear that the phenomena of the Fresnel diffraction cannot be explained by purely corpuscular considerations. It is necessary to attribute to the light quanta properties of phase and coherence similar to those of the waves of the classical theory.[5]

[1] The publication of this paper, written in 1924, was delayed because the authors were busy with other work. The recent discovery made by Davisson and Germer (*Nature*, **119**, p. 558, 1927) gives to the problem of corpuscular diffraction a new interest and importance.

[2] P. S. Epstein and P. Ehrenfest, these PROCEEDINGS, **10**, p. 133, 1924.

[3] Cf., for instance, *Enzyklopädie der Math.*, Wiss.

[4] M. Planck, "Theorie der Wärmestrahlung," Formula (64). The factor 2 in Planck's formula arises from his considering a perfectly reflecting element, while we have a perfectly absorbing one.

[5] Since this was written, the work of de Broglie and Schroedinger has brought us much nearer to the solution of these problems.

ABSOLUTE INTENSITIES IN THE HYDROGEN-CHLORIDE ROTATION SPECTRUM

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The development of new quantum theories which purport to furnish a means for the prediction of the absolute intensities of spectral lines makes it important to determine these intensities experimentally in such cases as may be theoretically treated. One of these few is the pure rotation spectrum as, for example, that of hydrogen chloride recently determined in absorption by Czerny.[1] This spectrum was used by Tolman and Badger[2] in the calculation of integral absorption coefficients, and so for the determination of the experimental B_{ij}'s or the probabilities of transition from one energy state of rotation to the next higher in the presence of radiation which may be absorbed. Since, however, this spectrum was investigated with a spectrometer of not very great resolving power, this process may have led to somewhat inaccurate results. In the present article are described new experimental measurements on the same spectrum, and an improved method whereby they are used to determine absolute absorption coefficients.

If the absorption is measured at several pressures, keeping the path length constant, an indirect method can be used for evaluating $\int \alpha(\nu)d\nu$, which avoids the difficulties due to low resolving power. Suppose that the intensity of the background radiation used in the absorption experiments is the function of wave-length $I_0(\lambda)$. If now the center of the spectrometer slit is set on the wave-length λ_s, radiation of other wave lengths between the limits of say $\lambda_s + S$ and $\lambda_s - S$ will be falling on the thermocouple due to the finite slit width. We may make the reasonable assumption that the intensity of such light of wave-length $\lambda_s + \delta$ will

be given by the product of $I_0(\lambda_s + \delta)$ and of $f(\delta)$ a function characteristic of the spectrometer. Thus at this setting the total light falling on the thermocouple is given by

$$D = \int_{-S}^{+S} I_0(\lambda_s + \delta) f(\delta) d\delta \qquad (1)$$

and the observed galvanometer reading at this setting will be a measure of this quantity. At the same setting of the spectrometer, but with HCl in the absorption cell, the deflection will be a measure of $\int_{-S}^{+S} I(\lambda_s + \delta)$-$(\delta)d\delta$ where $I(\lambda)$ represents the intensity distribution in the new spectrum.

Now the difference in galvanometer deflections at a given setting, with the absorption cell evacuated and again when filled with gas, will be given by the following equation.

$$A = \int_{-S}^{+S} [I_0(\lambda_s + \delta) - I(\lambda_s + \delta)] f(\delta) d\delta. \qquad (2)$$

This quantity may be measured at several spectrometer settings, plotted as a function of λ_s, and a graphical integration will give, if we expand in δ and then group terms in powers of δ,

$$\int_{\lambda_1}^{\lambda_2} A d\lambda_s = \int_{\lambda_1}^{\lambda_2} \int_{-S}^{+S} \left\{ [I_0(\lambda_s) - I(\lambda_s)] + \left[\frac{dI_0(\lambda)}{d\lambda} - \frac{dI(\lambda)}{d\lambda} \right]_{\lambda=\lambda_s} \cdot \delta + \ldots \right\} f(\delta) d\delta d\lambda_s. \qquad (3)$$

If the absorption spectrum contains only one line which is narrow, on either side of this line the function I approaches I_0, and the two become practically identical at λ_2 and λ_1 if these limits are chosen sufficiently greater and smaller, respectively, than λ_0 the center of the line. At these limits the derivatives of the two functions will also become equal. Consequently all of the right-hand member of equation (3) vanishes, except as given in the following equation

$$\int_{\lambda_1}^{\lambda_2} A d\lambda_s = \int_0^{\infty} [I_0(\lambda) - I(\lambda)] d\lambda \int_{-S}^{+S} f(\delta) d\delta. \qquad (4)$$

Now since we are interested in the probability of absorption by an isolated molecule, let us define β as the fraction of energy absorbed per molecule encountered in the path of a parallel beam of radiation of unit cross section. Evidently the diminution in intensity as the light traverses a differential path is given by

$$-dI(\lambda) = I(\lambda)\beta(\lambda,p)dN \qquad (5)$$

since β will depend on the proximity of molecules to one another. It follows that

$$I_0(\lambda) - I(\lambda) = I_0(\lambda)(1 - e^{-\beta(\lambda,p)N}) \qquad (6)$$

when the beam has traversed a path containing N molecules. Combination with equation (4) yields the following relation

$$\frac{1}{\int f(\delta)d\delta}\int_{\lambda_1}^{\lambda_2} A d\lambda \backsimeq \int_0^{\infty} I_0(\lambda)(1 - e^{-\beta(\lambda,p)N})d\lambda. \qquad (7)$$

If we introduce the perfect gas law, differentiation with respect to pressure yields, if x is the length of the absorption vessel

$$\frac{1}{\int f(\delta)d\delta}\frac{d}{dp}\int_{\lambda_1}^{\lambda_2} A d\lambda \backsimeq \int^{\infty} I_0(\lambda) e^{-\beta(\lambda,p)\frac{px}{kT}}\left\{\frac{\partial\beta}{\partial p}\cdot\frac{px}{kT} + \beta(\lambda,p)\frac{x}{kT}\right\}d\lambda. \qquad (8)$$

And at zero pressure, if we may assume I_0 constant across the relatively narrow absorption line

$$\frac{kT}{xI_0(\lambda_0)\int f(\delta)d\delta}\frac{d}{dp}\int_{\lambda_1}^{\lambda_2} A d\lambda \backsimeq \int_0^{\infty} \beta(\lambda, o)d\lambda. \qquad (9)$$

The left-hand member of the equation is experimentally determinable. $\int A d\lambda$ is defined above. The quantity $I_0\ (\lambda_0)\int f(\delta)d\delta$ is measured by the galvanometer deflection when the spectrometer is set on λ_0 provided I_0 may be regarded as linear across the slit width, as may be seen from equation (1).

Now the ordinary absorption coefficient α, defined for atmospheric pressure with the path expressed in centimeters, is evidently related to β by the expression given below, provided the *integral* absorption coefficient would be unchanged in value if the effect of intermolecular forces could be decreased to zero.

$$\int \alpha(\lambda)d\lambda = n\int \beta(\lambda, o)d\lambda = \frac{p}{kT}\int \beta(\lambda, o)d\lambda \qquad (10)$$

where n is the number of molecules per cubic centimeter under the conditions of the measurement of α.

We have made a determination of the absorption of hydrogen chloride in the neighborhood of 80μ, at four pressures in a cell of 77 cm. path, closed with quartz windows. Our vacuum spectrometer employed a plane echlette grating of 1.636 mm. spacing, consisting of a stack of glass plates of equal thickness. These were arranged in step fashion and the polished edges formed the reflected surface of the grating. The spectrometer had slits 1.25 mm. wide and a focussing collimating mirror of 50 cm. focal length.

Figure 1 indicates the galvanometer deflection plotted against the spectrometer setting when the absorption cell was evacuated, and when filled to 2.5, 5, 10 and 20 cm. pressure of HCl gas. Each set of observations was repeated at least once with three exceptions. A small figure adjacent to a point indicates that two observations chanced to coincide. Through each set of points is drawn the most reasonable curve. It will be noted that the origin of ordinates has been successively displaced for the series of curves, for the purposes of clarity. For the observations beyond about 91μ the sensitivity of the apparatus was considerably increased, but on the plot all the deflections are reduced to the same scale. One may obtain an idea as to the probable experimental error from the figure. In few cases was the spread of points much greater than the possible error of reading. An error may be present due to the presence of shorter wave-lengths in high orders. We believe that this must be small since the light path included 4 mm. of quartz which greatly diminished the intensity of waves shorter than 45μ, and the grating was adjusted to give a weak second order of wave-lengths about 45μ. Short infra-red radiation was almost perfectly eliminated.

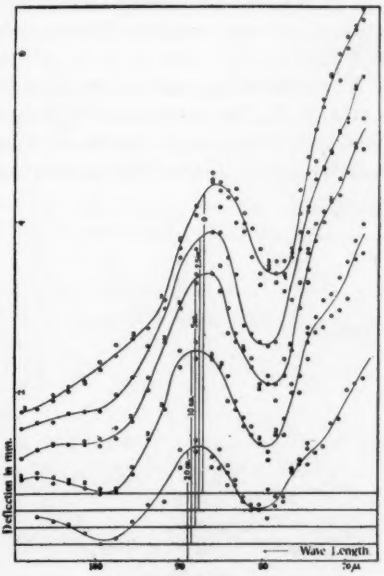

FIGURE 1
The intensity distribution in the background and absorption spectra.

In figure 2 the solid lines represent a plot of the differences in ordinate for the curve with evacuated cell and the other curves in succession of figure 1; in other words a plot of A, of the preceding discussion, against λ_2. Since, however, we have here three absorption lines which are incompletely resolved, it is necessary to divide the area under the solid curves into such parts as would be expected if it were possible to examine each line individually in the absence of others. The dotted lines indicate how this was done on the basis of assumptions which appear reasonable. In the upper corner of the figure are plotted the areas under the dotted curves for the line at 80.4μ as a function of pressure. This line is the one due to an increase in quantum number from 5 to 6. One may note several indications that the absorption lines broaden very appreciably with increase in pressure, among them being the shape of the last mentioned

curve which does not flatten out as rapidly at higher pressures as would be required for a constant width of line.

The tangent to this curve at the origin, which determines the value of β, is of course dependent on the division of the areas under the absorption curves. We believe, however, that the value which we have determined is not in error by more than ten per cent. We have found for n(76 cm. 22°)$\int\beta(\lambda,0)d\lambda$ the value 1.10×10^{-4} cm. Since the line is relatively narrow we may consider $d\lambda/d\nu$ constant across the line and obtain for $n\int\beta(\nu,0)d\nu$ the value 5.12×10^{10} sec.$^{-1}$.

The method for calculating from the integral absorption coefficient the value of B_{ij}, the average probability of transition from the initial to the final state with the absorption of radiation, has been indicated by Tolman and Badger.[2] Taking into account our present definition of β, and using the *a priori* probabilities for the respective quantum states given by the new theories, namely $2(i + 1/2)$, where i is the quantum number of the state, we obtain for $B_{5,6}$ the value 4.7×10^{16}.

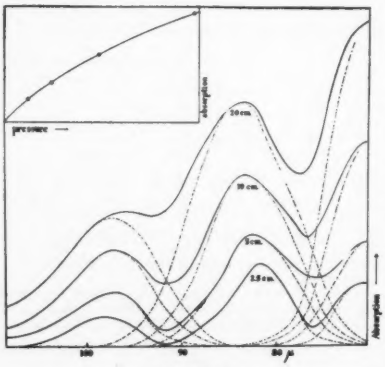

FIGURE 2
The absolute absorption curves.

In the new quantum theory developments the rotating molecule has received considerable attention and intensity relations have been derived in two different ways[3,4] involving the methods of Born, Heisenberg and Jordan; and of Schrödinger, respectively. The results are expressed in slightly different ways but when combined with the appropriate factors they seem both to lead to an expression for b_{ij}, the probability of absorption in unit density of radiation, of the following form

$$b_{ij} = \frac{8\pi^3\mu^2}{3h^2}\left(\frac{i+1}{2i+1}\right).$$

In this relation μ is an electric moment. If we may use the electric moment obtained from the dielectric constant by means of the Debye classical equation, b_{ij} may be evaluated. Substituting the value 1.034×10^{-18} c.g.s.u. which Zahn[5] obtained from his investigation on the dielectric constant of HCl, we obtain for $b_{5,6}$ the result, 1.12×10^{18}.

TABLE 1

LINE NO.	n(76 CM. 22°) $\int\beta(\nu,0)d\nu$	$B_{5,6}$ (EXPT.)	$b_{5,6}$ (THEORET.)
6	5.12×10^{10}	4.7×10^{16}	1.12×10^{18}

We have tabulated for comparison the probability of transition predicted by theory and that which is determined by experiment. Certainly the theoretical value fails to agree in magnitude with the experimental one by an amount much greater than the possible experimental error.

One may say, perhaps, that some factor must still be introduced in the theoretical expression to obtain the correct magnitude of b_{ij}; and the experimental observations offer a means of evaluating this. But, unfortunately, the theoretical probabilities do not have even the right relative values. They decrease with quantum number while for the experimental values Tolman and Badger found a decided increase. The absolute values which they calculated may be in error for the reasons given above, but more perfect resolution would be expected to increase the trend they observed rather than to eliminate it. It would seem, therefore, that the predictions of the new quantum theory, while they may apply to some ideal system, do not describe the conditions we have experimentally observed in the case of hydrogen chloride.

In conclusion we wish to express our indebtedness to the Carnegie Institution of Washington for funds which made this work possible.

[1] Czerny, *Zeits. f. Physik*, **34**, 227 (1925).
[2] Tolman and Badger, *Phys. Rev.*, **27**, 383 (1926).
[3] Dennison, *Phys. Rev.*, **28**, 318 (1926).
[4] Reiche, *Zeits. f. Physik*, **41**, 453 (1927).
[5] Zahn, *Phys. Rev.*, **24**, 400 (1924).

NOTE ON "PENDULUM" ORBITS IN ATOMIC MODELS

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On the simple Bohr theory the orbit of an electron moving in a central field of force about the nucleus is designated by two quantum numbers n and k, of which the first is called the principal quantum number and the second the azimuthal or auxiliary quantum number. These numbers are allowed to take all integral values (for a given orbit $k \leq n$) except zero. It will be seen that for $k = 0$ we get an orbit which is a straight line passing through the nucleus. This type of orbit is commonly known as a "pendulum" orbit and has been usually ruled out of the system of actual orbits because it involves collision of the electron with the nucleus. Nevertheless the fact that the *energy* of an electron orbit under the conditions specified above depends only on the principal quantum number and not on the azimuthal quantum number suggests the possibility of getting

quantized pendulum orbits (in the case of hydrogenic atoms at any rate) which have the correct energy values even though their physical possibility is open to question. In fact the recent tendency in modern atomic theory (as, for example, the matrix theory of Heisenberg and Born) to get away from pictures in space and time would seem to emphasize the value of utilizing for purposes of calculation the *simplest possible* orbits which have the correct energy values.

Pendulum orbits have been investigated by J. W. Nicholson.[1] He showed that if we write down the quantum condition for straight line motion, viz., $\oint m\dot{x}dx = nh$, substitute therein from the energy equation, disregarding the relativity correction, and integrate from $x = 0$ to $x = a$ we arrive at the usual Balmer energy value, viz., $W = -2\pi^2N^2e^4m/n^2h^2$. The next step was to employ the energy equation for the relativity case, which is as follows:

$$m_0c^2\left[\frac{1}{\sqrt{1-\dot{x}^2/c^2}} - 1\right] - \frac{Ne^2}{x} = W \qquad (1)$$

where m_0 is the rest mass of the electron, e its charge, c the velocity of light, W the energy and N the number of charges on the nucleus. The result of the subsequent analysis appears to be that to a first approximation W comes out to have the same value as in the previous simpler case, i.e., we get correctly quantized orbits. However, inspection shows that there is a serious error involved in Nicholson's reasoning. In the quantum condition he used the rest mass m_0 instead of the varying mass m.[2] It then becomes important to carry through the analysis correcting this error to see what influence it has on the result.

Proceeding as usual[3] we have for the momentum

$$p_x^2 = 2m_0W + W^2/c^2 + 2(m_0Ne^2 + WNe^2/c^2)/x + N^2e^4/c^2x^2 \qquad (2)$$

whence the quantum conditions becomes

$$\oint \sqrt{A + 2B/x + C/x^2}\, dx = nh \qquad (3)$$

where

$$\left.\begin{aligned} A &= 2m_0W + W^2/c^2 \\ B &= m_0Ne^2 + WNe^2/c^2 \\ C &= N^2e^4/c^2 \end{aligned}\right\}. \qquad (4)$$

As usual the integration is to be conducted from the larger of the two roots of the radicand to the smaller and back again. Since B and C are both positive quantities and A alone is negative, one of the roots of the radicand is positive and the other negative, i.e., the electron must pass

through the nucleus and penetrate a certain distance on the other side before $p_x = 0$. The difficulty is that the radicand becomes infinite for $x = 0$ and hence the integral is an infinite integral. Examination discloses that the integral does not converge as $x = 0$; hence the quantum condition as stated ceases to have a meaning.

The question remains under what conditions a pendulum-orbit quantized according to $\oint p_x dx = nh$ is possible. Independently of the failure of the integral to converge the idea of the passage of the electron through the nucleus may be distasteful to some. There is a possible way of avoiding this, namely, by the introduction of a repulsive force (in addition to the inverse square attractive force) operative only in the immediate vicinity of the nucleus. This assumption is not so fearfully arbitrary, for the work on α-particle scattering has indicated clearly that the inverse square law breaks down in the close vicinity of the nucleus. Of course, the exact form for a law of the kind indicated is a matter requiring closer investigation. For the purpose of the present work, however, the writer has thought it valuable to see the effect of using the simplest possible law, namely, an inverse cube force. The mathematical analysis in this case is far simpler than in the cases of higher power force laws, and from the result we should be able to infer qualitatively the effect of introducing a more complicated law.

Replacing in equation (1) Ne^2x by $Ne^2/x - \alpha e^2/x^2$ where α is a coefficient, equation (3) becomes

$$\oint \sqrt{A + 2B/x + C'/x^2 + D_1/x^3 + D_2/x^4}\, dx = nh \qquad (5)$$

where A and B are as given in (4) and

$$\begin{aligned} C' &= N^2e^4/c^2 - 2m_0e^2\alpha - 2We^2\alpha/c^2 \\ D_1 &= -2Ne^4\alpha/c^2, \quad D_2 = e^4\alpha^2/c^2. \end{aligned} \qquad (6)$$

The limits of integration are obtained as the roots of the equation

$$W + Ne^2/x - \alpha e^2/x^2 = 0. \qquad (7)$$

These roots are:

$$\left.\begin{aligned} x_{\max.} &= -Ne^2/W - \alpha/N \\ x_{\min.} &= \frac{\alpha}{N}(1 - \alpha W/N^2e^2) \end{aligned}\right\} \qquad (8)$$

both to the second approximation (i.e., $\alpha << e^2/W$). Since D_1 and D_2 are correction terms we can evaluate (5) by expanding by the binomial theorem. Then

$$nh = \int \sqrt{A + 2B/x + C'/x^2}\, dx + \int \frac{1}{2}(A + 2B/x + C'/x^2)^{-1/2}(D_1/x^3 + D_2/x^4)dx - \frac{1}{8}\int (A + 2B/x + C'/x^2)^{-3/2}(D_1/x^3 + D_2/x^4)^2 dx + \ldots \quad (9)$$

Since we do not intend to restrict C' to negative values we do not employ the method of complex integration. We have

$$\int \sqrt{A + 2B/x + C'/x^2}\, dx = -2\sqrt{X_{\min.}} + \frac{2B}{\sqrt{-A}} \arcsin\left[-\frac{Ax + B}{\sqrt{B^2 - AC'}}\right]_{x_{\min.}}^{x_{\max.}} + \begin{cases} \dfrac{2C'}{\sqrt{-C'}} Z_1, & \text{for } C' < 0 \\ (-2)\sqrt{C'} Z_0, & \text{for } C' > 0. \end{cases} \quad (10)$$

In (10) we have set $X = Ax^2 + 2Bx + C'$, whence $X_{\min.} = Ax^2_{\min.} + 2Bx_{\min.} + C'$. Moreover we also have

$$\left.\begin{aligned} Z_0 &= \log\left[\frac{\sqrt{X} + \sqrt{C'}}{x} + \frac{B}{\sqrt{C'}}\right]_{x_{\min.}}^{x_{\max.}} \\ Z_1 &= \arcsin\left[\frac{Bx + C'}{x\sqrt{B^2 - AC'}}\right]_{x_{\min.}}^{x_{\max.}} \end{aligned}\right\}. \quad (11)$$

Proceeding similarly with the first correction term we have

$$\frac{1}{2}\int (A + 2B/x + C'/x^2)^{-1/2}(D_1/x^3 + D_2/x^4)dx$$

$$= \frac{Z_1}{C'\sqrt{-C'}}\left[-BD_1 - \frac{D_2}{2}\left(\frac{3B^2}{C'} - A\right)\right] + \frac{\sqrt{X_{\min.}}}{C'x_{\min.}}\left[D_1 - \frac{D_2}{2}\left(\frac{3B}{C'} - \frac{1}{x_{\min.}}\right)\right] \text{ if } C' < 0$$

$$= \frac{Z_0}{C'\sqrt{C'}}\left[BD_1 - \frac{D_2}{2}\left(\frac{3B^2}{C'} - A\right)\right] + \frac{X_{\min.}}{C'x_{\min.}}\left[D_1 - \frac{D_2}{2}\left(\frac{3B}{C'} - \frac{1}{x_{\min.}}\right)\right] \text{ if } C' > 0 \quad (12)$$

Investigation of the order of magnitude of the correction terms D_1 and D_2 indicates that it will not be necessary for the approximation desired in this work to use the second order correction term. Substitution of the limits and replacement of A, B, C', D_1, D_2 by their values as given in (4) and (6) yield finally

$$\frac{2\pi e^2}{c}\left[-1+(1+W/m_0c^2)^{-2}\right]^{-1/2}\cdot$$
$$\left[1-\frac{1}{\pi}\left\{-\frac{2W}{m_0c^2}(1+(N-1)\lambda)\right\}^{1/2}\right]=nh+\Psi \quad (13)$$

where Ψ represents a correction term different according as $C'<0$ or $C'>0$. Thus we have

$$\Psi C'_{<0}=Ne^2/c\cdot[1+(N-1)\lambda]^{1/2}\cdot[2+2/N(1-\lambda)-1/2N^2(1-\lambda)+3\lambda/2N(1-\lambda)^2]$$
$$+\frac{Ne^2/c}{(\lambda-1)^{1/2}}\cdot\left[\pi/2-\text{arc sin}\,\frac{N-2}{N}\left(1+\frac{2}{(N-2)\lambda}\right)\right]\cdot$$
$$[2(\lambda-1)-2\lambda/(1-\lambda)-3\lambda^2/8(1-\lambda)^2] \quad (14)$$

and

$$\Psi_{C'<0}=Ne^2/c\cdot[1+(N-1)\lambda]^{1/2}\cdot[2+2/N(1-\lambda)-1/2N^2(1-\lambda)+3\lambda/2N(1-\lambda)^2]$$
$$\frac{-Ne^2/c}{(1-\lambda)^{1/2}}\cdot[2(1-\lambda)+2\lambda/(1-\lambda)+3\lambda^2/8(1-\lambda)^2]\log[1+2(1-\lambda)^{1/2}/N\lambda\cdot\{1+N(1-\lambda)^{1/2}\}] \quad (15)$$

In the expressions (14) and (15) we have set $\lambda=2m_0c^2\alpha/N^2e^2$. The quantity λ is of the order of unity, and it is clear that for (14) $\lambda>1$, while for (15) $\lambda<1$.

Now returning to (13) we have, after the usual transpositions, the following expression for the energy

$$W=\frac{-2\pi^2N^2m_0e^4}{n^2h^2}\{1-2(\Psi+2Ne^2/c\cdot\sigma)/nh$$
$$-[(\Psi-6Ne^2/c\cdot\sigma)(\Psi+2Ne^2/c\cdot\sigma)+3\pi^2N^2e^4/c^2]/n^2h^2\} \quad (16)$$

wherein we set $[1+(N-1)\lambda]^{1/2}=\sigma$. In order that (16) should be equivalent to the Balmer formula with the addition of a correction term of the same sign and the same order as that of the relativity term, it is essential that we have

$$-2(\Psi+2Ne^2/c\cdot\sigma)-[(\Psi-6Ne^2/c\cdot\sigma)(\Psi+2Ne^2/c\cdot\sigma)+3\pi^2N^2e^4/c^2]/nh=\pi^2N^2e^4/c^2nh \quad (17)$$

whence we must have:

$$\Psi=-2Ne^2/c\cdot\sigma\{1+\pi^2Ne^2/c\sigma nh\cdot(1+4Ne^2\sigma/cnh)\}. \quad (18)]$$

Examination of (14) and (15) in connection with (18) shows that for $C' < 0$ it is in general not possible to find a value of λ such that the corresponding value of Ψ satisfies (18). However, this does prove always to be possible for $C' > 0$. In the particular case of the hydrogen atom where $N = 1$ and $\sigma = 1$, it develops that the proper value of λ is $\lambda = 0.179$ which corresponds to $\alpha = 0.25 \times 10^{-13}$. For hydrogen, then, we have

$$x_{\text{min.}} = 0.25 \times 10^{-13}[1 - 0.5 \times 10^{-13}\pi^2 m_0 e^2/n^2h^2]$$

or roughly 0.25×10^{-13} cm. This result cannot be looked upon as unreasonable, though unfortunately there is no experimental data available for comparison. However, from the expression for λ on page (5) it is seen that α varies as N^2 (though, of course, it will also depend on λ which will vary slightly with N). Hence $x_{\text{min.}}$ will increase roughly proportionally with N (for small values of N, at any rate). Actual calculation for the case of He($N = 2$) shows $x_{\text{min.}} = 0.62 \times 10^{-13}$ cm. while for the case of Al($N = 13$) we get $x_{\text{min.}} = 2 \times 10^{-13}$ cm. This latter value is at any rate qualitatively in agreement with Bieler's value for the effective radius of the Al nucleus, namely 3.3×10^{-13} cm. as estimated from the analysis of experiments[4] on α-ray scattering by Al nuclei. Unfortunately, there is no record of electron scattering at such close distances. Thus Schonland[5] finds that in the case of electron scattering by Al foils the inverse square law holds down to 1.8×10^{-11} cm. In any case there seems to be no experimental data which would militate *against* the assumption underlying the above work.

It may be pertinent to introduce here a few remarks concerning the relation between the kind of pendulum orbit used in this work and the newer theories of atomic structure. In the Schrödinger wave mechanics[6] the azimuthal quantum number has been put equal to $l + 1$, where l can take only the values 0, 1, 2, 3, ... Hence $l = 0$ would not lead to the vanishing of the angular momentum, and so Schrödinger concludes that paths for which the angular momentum vanishes do not exist. The difficulty with this conclusion, as it seems to the present writer, is that there seems no definite assurance that the angular momentum of the electron in an actual orbit must be represented by the quantum number $l + 1$. More generally, the Schrödinger theory does not fix electron orbits in time and space as we have previously understood them; it fixes only the value of a certain function (the eigen-funktion ψ) in the configuration space. It thus seems that the new theory affords a considerable amount of latitude in the choice of electron orbits corresponding to a given distribution of the ψ function. The same comment applies to the matrix mechanics of Born and Heisenberg, which is mathematically equivalent to the wave mechanics. If modern atomic theory is going to retain atomic models at all (which seems likely if only for the pictorial advantage afforded by them) then all

that is required of an electron orbit in such a model is that it shall have the proper energy value and be of the right order of magnitude for atomic dimensions. It may well be that pendulum orbits which satisfy these conditions will still prove useful in atomic theory.

[1] J. W. Nicholson,, *Phil. Mag.*, **45**, 804 (1923).

[2] This fact was first called to the attention of the present writer by Prof. A. E. Ruark.

[3] A. Sommerfeld, *Atombau und Spektral linien*, 3rd German ed., page 735.

[4] E. S. Bieler, *Proc. Roy. Soc.*, **105**, 434 (1924).

[5] B. F. J. Schonland, *Proc. Roy. Soc.*, **113**, 87 (1926).

[6] E. Schrödinger, *Ann. Physik*, **79**, 371 (1926). The number l here used corresponds to n in the paper referred to, in conformity with more recent usage.

MEASUREMENT OF THE MO.K DOUBLET DISTANCES BY MEANS OF THE DOUBLE X-RAY SPECTROMETER

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The doublet which should be present in the $K\beta$ radiation has only been observed in the case of a few elements; between $Z = 41$ and $Z = 50$.[1] Their separation is so small that they appear as a single line except with an instrument of high resolving power.

We have recently found that the double X-ray spectrometer possesses high resolving power when properly arranged. We have obtained a considerable separation of the Kβ doublet of Mo as shown in figure 3.

The geometry of the arrangement used will be easily understood from figure 1. The two slits between the X-ray tube and the crystal Z are quite wide (1.5 mm.) so that a divergent beam comes through to crystal A. Crystal A may be regarded as the collimator and crystal B as the analyzer. If these crystals are nearly perfect, such as split calcite, only one wave-length is reflected at a given angle of incidence. This is not strictly true as it has been found from previous experimental work that some energy is reflected at about 4″ of arc each side the proper angle for reflection of a given wave-length, λ.

A radiation of certain wave-length, say λ_1 represented by full lines in figure 1, falls on crystal A at proper angle θ for reflection. Any other wave-length proceeding along same path will not be reflected. But radiation of another wave-length such as λ_2 of the figure coming through the slits at a different angle $(\theta + d\theta)$ will be reflected at its proper angle

from crystal A to crystal B. That is if two radiations slightly differing in wave-length are present two parallel beams will strike crystal B at slightly different angles of incidence. These two beams λ_1, λ_2 represent in these experiments the Kα doublet in one instant and the Kβ doublet in the other.

The position of crystal B that will reflect λ_1 is shown by the full line in the figure. At this position the λ_2 radiation will not be reflected from B. If now the crystal be rotated through an angle $2d\theta$ to position represented by the broken lines, the λ_2 radiation will be reflected and not the λ_1. The angle $2d\theta$ represents the difference of the angles that the two beams make with surface of crystal B. If $d\theta$ is not too small separate rocking curves are obtained for each radiation (λ_1, λ_2). If the angle $d\theta$ is too small, that is, if λ_1 and λ_2 are too nearly of same wave-length, the two rocking curves merge into one curve of greater width.

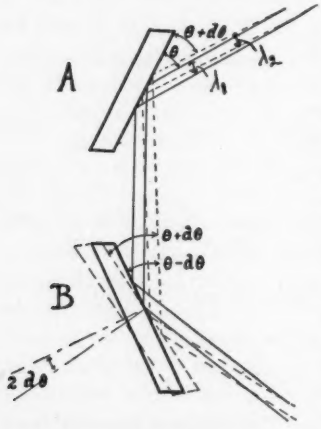

FIGURE 1

Crystal A was mounted in the usual manner at the center of the spectrometer table. Crystal B was provided with a lever arm and tangent screw that permitted small angles of turn to be measured to one-half second of arc. The slits were quite wide, 1.5 mm. or more. The distance between slits was 50 cm. It was found that the width of rocking curve was closely independent of horizontal slit width. An important matter, however, was the vertical height of slits. With slits a centimeter or more in height the rocking curves were quite wide, but their width progressively decreased as vertical height decreased. The vertical height finally used was 1.75 mm. That is, the cross-section of beam falling on A was 1.5 mm. by 1.75 mm. This property that the horizontal slit width does not affect the width of rocking curves is a useful one as sufficient intensity of radiation is obtained to permit quite accurate measurements.

To obtain the same resolving power with a single X-ray spectrometer having slits 50 cm. apart would require very narrow slits, about 0.001 cm. The energy would be too small for accurate measurement. This arrangement of the double X-ray spectrometer increases the resolving power at least ten times over that of the single for the same energy received in the ionization chamber.

The rocking curves obtained are shown in figures 2 and 3. Figure 2

represents the $K\alpha_1\alpha_2$ doublet. The angular separation is about fourteen times the width of curve at half-maximum. The separation of $2d\theta = 292''$ of arc is the angle read on crystal B. It is twice the separation for a single crystal. The better determination of the α_1,α_2 wave-lengths gives $d\lambda = 0.0043$ Å. The angular separation corresponding to this is $147''$. The above determination gives $\frac{1}{2}(292'') = 146''$. The agreement is well within the errors of measurement in both cases.

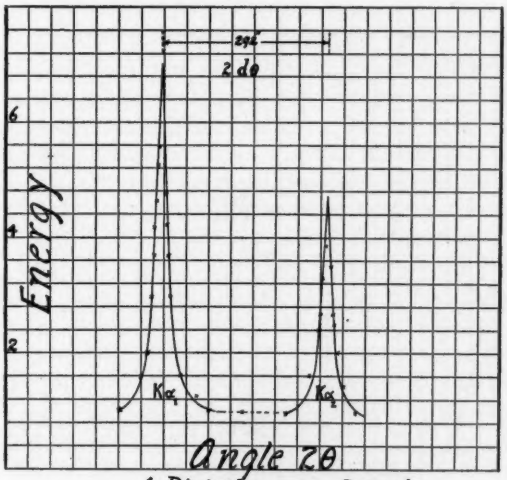

FIGURE 2

The $K\beta$ doublet and the $K\gamma$ line are shown in figure 3. The separation of $\beta - \gamma$ of $\frac{1}{2}(760'') = 380''$ agrees with that obtained from wave-length measurements. The β_1, β_2 doublet is separated by $2d\theta = 40''$ or $d\theta = 20''$. The corresponding wave-length separation is $d\lambda = 0.00058$ Å. Recent reliable determinations of these wave-lengths give β_1, β_2 as 0.630791 Å and 0.631354 Å, respectively.[2] The corresponding doublet distance is 0.000563 Å.

The $K\gamma$ line is, of course, a doublet also, but it has not yet been separated. The $K\gamma$ curve is wider at half-maximum than the $K\beta_1$, which indicates it is not a single structure. Could the resolving power be increased this would undoubtedly be separated into a doublet.

A consideration of the geometry of the double reflection shows that it is possible to obtain a parallel beam of X-rays of a single wave-length selected out from the continuous X-ray spectrum. In this case a beam having wave-length lying between λ and $\lambda + d\lambda$ will be reflected from crystal A. But only radiation of a given λ will be selected out of this

bundle by crystal *B*. This beam will be parallel and monochromatic within the tolerance angle of the crystal (about 4″).

A number of interesting effects have been observed in the case of the radiation from elements of lower atomic number, such as the effect of chemical combination on the structure of the absorption limit observed by Bergengren and Lindh as well as its effect on the structure of the emission lines.[3]

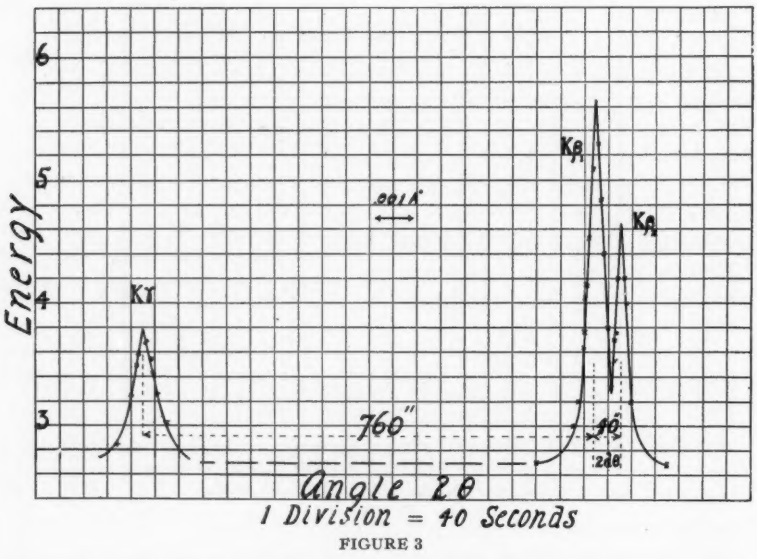

FIGURE 3

Another effect of considerable importance is the fine structure of the emission lines and its dependence on excitation voltage.[4] This arrangement of the double X-Ray spectrometer should make possible the investigation of these and other effects in the case of elements of higher atomic number.

[1] Compton, X-Rays and Electrons.
[2] Allison and Armstrong, *Phys. Rev.*, Dec., 1925.
[3] Siegbahn, *Spectroscopy of X-Rays*, p. 142 and p. 99.
[4] Siegbahn, *Ark. Mat. Ast. O. Fys.*, **18**, No. 18.

THE STRUCTURE OF THE HELIUM ATOM. I

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The attempts to calculate the spectrum of helium from the wave equation of mechanics have been based on the method of perturbations. The actual problem can presumably not be solved explicitly; but we approximate to it by a soluble problem, and determine the correct solution by successive approximations from this. The success of the method depends entirely on finding a soluble problem to serve as the unperturbed solution, which is a sufficiently close approximation to the real case; for the closer it is, the faster the process converges. Little attention has been paid to this part of the question, with the result that the solutions so far obtained,[1] though qualitatively interesting, are quantitatively far from the truth. In the present note, a new method of finding a soluble approximation is presented. This is applied to the problem of helium, where even the soluble, unperturbed problem gives results in close agreement with experiment, the computed ionization potential differing from the true value by less than a per cent,* indicating that the higher approximations will converge with great rapidity. The method seems to be of far-reaching application, and its usefulness in the problems of the higher atoms, and of molecular structure, is discussed.

1. *The Method of Perturbations.*—The problems in which we are interested are those with more than one degree of freedom, so that the wave equation is a partial differential equation; for the solution of the case of one degree of freedom can be carried out, to any desired approximation, by well-known methods,[2] and we may regard any problem as solved when it is reduced to a set of one-dimensional problems. If the variables can be separated, this can be done at once; so that we must consider particularly those problems where the variables are not separable. The method so far used in such cases has been to leave out, for the unperturbed problem,

* *Note Added in Proof:* More accurate calculation of the unperturbed problem, carried out since the paper was sent in, has shown that the preliminary results of table 1 gave an exaggerated idea of the closeness of the agreement with experiment. Improvement of the arithmetical accuracy has raised the ionization potential from a slightly low value to about two per cent above the correct amount. In addition, Kramers' approximate method of solution for the central field problem has been replaced by an actual numerical integration of the equation, and this introduces an additional discrepancy of two to three per cent, in the same direction, so that the correct solution for the ionization potential of the unperturbed problem is five or six per cent greater than the experimental value. The correction introduced by the next approximation is, however, of the proper sign to reduce the ionization potential. For the excited level, the term is also increased by the changes, bringing it closer to the experimental value.

all those terms in the energy which prevent the separation of variables, regarding all these as perturbative terms, and solve the remaining problem by separation. Since these are, in general, the terms representing the interaction between electrons, it is obvious that the unperturbed problem will be a very poor approximation to the real case. We proceed in quite a different way, making no attempt to separate variables at all.

The method can be fully explained with respect to a problem of two degrees of freedom. We let the two coördinates be x_1, x_2, and then have the wave equation

$$\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2\psi(x_1x_2)}{\partial x_1^2}+\frac{\partial^2\psi(x_1x_2)}{\partial x_2^2}\right)+(V(x_1x_2)-E)\psi(x_1x_2)=0. \quad (1)$$

The first step is to set up the equation

$$\frac{-h^2}{8\pi^2 m}\frac{\partial^2 u(x_1x_2)}{\partial x_1^2}+(V(x_1x_2)-\epsilon(x_2))u(x_1x_2)=0. \quad (2)$$

In this equation x_2 is to be regarded merely as a parameter, so that it is really an ordinary differential equation, in the one variable x_1. Being an ordinary differential equation, we can solve it, obtaining a set of characteristic functions $u_n(x_1x_2)$ corresponding to different characteristic numbers $e_n(x_2)$. In both of these, x_2 appears still as a parameter. Next we form the set of equations

$$\frac{-h^2}{8\pi^2 m}\frac{d^2v_n(x_2)}{\partial x_2^2}+(\epsilon_n(x_2)-\eta_n)v_n(x_2)=0, \qquad n=0,1,\ldots. \quad (3)$$

These are ordinary equations, so that each can be solved; the solution of the nth may be written as a set of characteristic functions $v_{nm}(x_2)$, $m = 0, 1, \ldots.$, corresponding to the characteristic numbers η_{nm}, $m = 0, 1, \ldots$ We now take as the unperturbed characteristic functions and numbers of our original problem (1) the quantities

$$\begin{aligned}\psi^0_{nm}(x_1x_2) &= u_n(x_1x_2)v_{nm}(x_2),\\ E^0_{nm} &= \eta_{nm}.\end{aligned} \quad (4)$$

It is easily shown that the functions ψ_{nm} are orthogonal and can be normalized. The functions $u_n(x_1x_2)$, regarded as functions of x_1, are characteristic solutions of an ordinary differential equation, and hence are orthogonal; we can then multiply by functions of x_2, without interfering with their property of being solutions of (2), so as to normalize them for each value of x_2. We assume this done:

$$\int u_n(x_1x_2)u_m(x_1x_2)dx_1=\delta_{nm}, \quad \text{for any } x_2. \quad (5)$$

Likewise the functions $v_{nm}(x_2)$, in which m is regarded as the index,

are characteristic solutions of a differential equation in x_2; so that they are orthogonal, and can be normalized, by multiplication by constants:

$$\int v_{kn}(x_2)v_{km}(x_2)dx_2 = \delta_{nm}, \quad \text{for any } k. \tag{6}$$

Then we have

$$\begin{aligned}\int\int \psi^0_{nm}(x_1x_2)\psi^0_{kl}(x_1x_2)dx_1dx_2 &= \int\int u_n(x_1x_2)v_{nm}(x_2)u_k(x_1x_2)v_{kl}(x_2)dx_1dx_2 \\ &= \int dx_2 v_{nm}(x_2)v_{kl}(x_2)\int u_n(x_1x_2)u_k(x_1x_2)dx_1 \\ &= \int dx_2 v_{nm}(x_2)v_{nl}(x_2)\delta_{nk}, \quad (by(5)), \quad = \delta_{nk}\delta_{ml}, \quad (by\ (6)). \end{aligned} \tag{7}$$

Thus the ψ^0_{nm}'s are orthogonal and normalized and can properly serve as a set of characteristic functions.

Next we inquire what differential equation the ψ^0_{nm}'s satisfy. We write (2) with its indices n, (3) with its indices m, multiply (2) by $v_{nm}(x_2)$, (3) by $u_n(x_1x_2)$ and add. The result is

$$\frac{-h^2}{8\pi^2 m}\left(v_{nm}(x_2)\frac{\partial^2 u_n(x_1x_2)}{\partial x_1{}^2} + u_n(x_1x_2)\frac{\partial^2 v_{nm}(x_2)}{\partial x_2{}^2}\right) + (V(x_1x_2) - \eta_{nm})\psi^0_{nm}(x_1x_2) = 0. \tag{8}$$

Using (4), this may be written

$$\begin{aligned}\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2\psi^0_{nm}(x_1x_2)}{\partial x_1{}^2} + \frac{\partial^2\psi^0_{nm}(x_1x_2)}{\partial x_2{}^2}\right) + (V(x_1x_2) - \eta_{nm})\psi^0_{nm}(x_1x_2) \\ = \frac{-h^2}{8\pi^2 m}\left(2\frac{\partial u_n(x_1x_2)}{\partial x_2}\frac{\partial v_{nm}(x_2)}{\partial x_2} + u_{nm}(x_2)\frac{\partial^2 u_n(x_1x_2)}{\partial x_2^2}\right).\end{aligned} \tag{9}$$

If the right side of equation (9) were zero, ψ^0_{nm} would be a solution of the original equation (1), with characteristic numbers η_{nm}. This, in general, will not be true. Nevertheless, from the physical nature of the method, as well as from the actual cases to be discussed later, it appears that (4) forms a decidedly good approximation to a solution of (1). Hence we may assume that the right side of (9), though not zero, is small; we have a solution of an equation near the desired one, though not exactly it; and we may apply a method essentially like Schrödinger's[3] to find the successive approximations to the actual solution. We develop the right side of (9) in a series of the orthogonal functions ψ^0_{nm}, and the rest of the procedure is almost exactly like Schrödinger's, so that it would hardly pay to present the details. In the case where the two degrees of freedom represent identical systems, we make a change of variables, as Heisenberg[4] has done, and obtain the resonance phenomena just as he does. The essential advantage of the present method lies in the accuracy of its unperturbed solution, not in any difference in the way of carrying out higher approximations.

2. *Application to Helium.*—The wave equation for the helium atom is

$$\frac{-h^2}{8\pi^2 m}(\Delta_1^2\psi + \Delta_2^2\psi) + \left(\frac{-2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}} - E\right)\psi = 0. \quad (10)$$

Here there are six variables, the coördinates of the two electrons. Δ_1^2 represents the sum of the second partial derivatives with respect to the coördinates of the first electron, Δ_2^2 the corresponding sum for the second; r_1 and r_2 are the distances of the first and second from the nucleus, r_{12} the distance between. First, corresponding to (2), we set up the equation

$$\frac{-h_2}{8\pi^2 m}\Delta_1^2 u(x_1y_1z_1x_2y_2z_2) + \left(-\frac{2e^2}{r_1} + \frac{e^2}{r_{12}} - \left(\epsilon(r_2) + \frac{2e^2}{r_2}\right)\right) u(x_1y_1z_1x_2y_2z_2) = 0. \quad (11)$$

With r_2 fixed, this is the equation for the problem of an electron in the field of two centers, one a charge $2e$ at the nucleus, the other a charge $-e$ at the fixed point $(x_2y_2z_2)$. In the absence of an external field, the energy levels of this problem will depend only on the distance apart of the centers (r_2) and not on the orientation, which is the reason for writing $\epsilon(r_2)$ instead of $\epsilon(x_2y_2z_2)$ in (11). This problem can be solved; we separate variables in elliptical coördinates in the well-known way. Then we take the functions $\epsilon_n(r_2)$, where n stands for the three quantum numbers of the problem, obtained from this solution and set up, corresponding to (3), the equations

$$\frac{-h^2}{8\pi^2 m}\Delta_2^2 v_n(x_2y_2z_2) + (\epsilon_n(r_2) - \eta_n)v_n(x_2y_2z_2) = 0. \quad (12)$$

These are the equations for the motion of an electron in the central fields whose potentials are given by $\epsilon_n(r_2)$, in which again we can separate variables, and obtain the solution with the characteristic numbers η_{nm}. It is a striking fact that this method leads to the problem of motion in a central field as the last step of the process; for it has, of course, been known for a long time that a central field could be set up,[5] such that the orbits in it gave energies in good agreement with experiment. The present method seems to be the mathematical justification of this process. In the ordinary case, we are interested only in the problem in which one electron is in the normal orbit. Then we wish, say, the states η_{0m}, $m = 0, 1, \ldots$. For these states, we need solve only the particular case of (12) in which $n = 0$; that is, all these orbits come from one single central field, as has been found in the work mentioned above. Consequently we need only the lowest energy level of (11), which greatly simplifies the actual work of calculation. For the states of helium in which both electrons are excited, we need other solutions of (11), and obtain different central fields for the various quantum numbers of the inner electron. The present method

obviously cannot give the separation between singlet and triplet terms as part of the unperturbed solution; we must go to the first approximation, just as Heisenberg does, to obtain these separations. We cannot identify η_{0m} and η_{m0} as two separate terms; if it should appear that they were really different, as seems likely from their quite different modes of calculation, we should not assign any physical meaning to the difference; it would be a result of faults in our method of setting up the unperturbed problem. The proper procedure in this case can easily be given, but it is not necessary to describe it here.

The actual calculation has been carried at present far enough to find the energy levels of the unperturbed system. The problem (11) of the motion of an electron in the field of two centers, cannot be solved explicitly; but since we need only the lowest energy level, as a function of the distance of separation, it is a comparatively simple matter to find the solution numerically. Using the method employed by Burrau[6] on the very similar problem of the hydrogen molecule-ion, this has been carried out with fair accuracy. The lowest energy level of this problem, regarded as a function of the distance between the charge $-e$ and the nucleus $2e$, or r_2, approaches $-4Rh$ when $r_2 = \infty$, and the problem is that of an electron in the field of nucleus $2e$; it approaches $-Rh$ when $r_2 = 0$, and the $-e$ neutralizes one of the two charges on the nucleus. For large r_2, it is approximately $-4Rh + e^2/r_2$, the sum of the energies required to remove the electron from its orbit to infinity against the combined action of the nucleus and the charge $-e$. As r_2 becomes smaller, the polarization energy from the second order Stark effect becomes appreciable, and is the only important correction to the function above for r_2 greater, say, than 1.5 times the radius of the first hydrogen orbit. For r_2 smaller than this, since the solution must approach the finite value $-Rh$, the development in inverse powers of r_2 becomes impossible. The function which we have just described is the one called $\epsilon_0(r_2) + 2e^2/r_2$ in (11). Subtracting $2e^2/r_2$ from this, we see that $\epsilon_0(r_2)$, which acts as the potential in the second part of the problem, approaches $-4Rh - e^2/r_2$ at large values of r_2, and $-Rh - 2e^2/r_2$ at small r_2. If we then write, in (12), $\epsilon_0(r_2) - \eta_{0m} = (\epsilon_0 + 4Rh) - (\eta_{0m} + 4Rh)$, the first bracket approaches $-e^2/r_2$ for large r_2, and $-2e^2/r_2 + 3Rh$ for small r_2. This is just the sort of potential we should expect to give the right answer. The energy levels of this problem are then the quantities $\eta_{0m} + 4Rh$; so that $\eta_{0m} = -4Rh +$ energy levels of electron in central field. The term $-4Rh$ obviously represents the energy required to remove the second electron after the first is taken away, since the problem as we have set it up is the problem of the whole atom. The characteristic values of the problem of potential $\epsilon_0(r_2) + 4Rh$ give directly the energies in the ordinary arc spectrum, referred to the limit of this spectrum as a normal.

The problem of the motion of an electron in the central field of potential $\epsilon_0(r_2) + 4Rh$ can be approximately carried out by the method of Kramers.[7] He shows that a good approximation is obtained by using the ordinary radial quantum condition of the older quantum theory, only substituting $(k-1/2)^2$ for k^2, where $k = 1, 2, 3, \ldots$ for $S, P, D, \ldots$, and by making the phase integral equal to $(n + 1/2)h$ instead of nh, where n is the old radial quantum number. This is easily carried out by the method of Fues (loc. cit.). We give in figure 1 the P and Q curves, in Fues's notation, for the central field derived from the problem (11). The principal emphasis in the calculations made so far has been on the S states. It is obvious from the curves that the essential parts of the potential curve for the P states, as well as the D and F, lie so far out that only the polarization term in $\epsilon(r_2)$ is of importance. Since these terms have been treated by Waller and Heisenberg (loc. cit.), and have been shown to lead to the correct energies of these states, it has not yet been thought necessary to obtain the potential accurately in this region. For the S states, the parabolas have been adjusted so as to give half integral quantum numbers. We give in table 1 the energy levels so obtained, and as experimental values the mean of the singlet and triplet S levels of helium, or in the normal state the singlet level itself, which are to be compared with the computed values. The agreement is very remarkable, especially in the normal state; it is quite within the limit of error of the arithmetical calculations, which have not yet been made very accurately. Since it is so close, it seems unquestionable that the first approximation will agree very well with the facts. The computation of this approximation is now being carried out; it is naturally rather laborious, since we must find the characteristic function by numerical integration of the equations (11) and (12), and perform mechanical quadratures of these. It is hoped to report on these calculations in a later paper.

TABLE 1*

	WAVE NUMBERS 1s	2s	QUANTUM DEFECTS 1s	2s
Singlet	198,289	32,032	0.256	0.149
Triplet		38,454		0.321
Mean	198,289	35,243	0.256	0.234
Calculated	197,200	34,200	0.254	0.208
	Ionization Potential:		Observed:	24.48 volts
			Calculated:	24.35 volts

3. *Other Applications.*—The method developed in the present paper yields immediately valuable qualitative information in many problems, although its quantitative applications would be more difficult. Two quite different methods of extending it to problems of more than two electrons suggest themselves. First, we could use a sort of telescoping method, solving first a problem in which all but one of the coördinates were held

fast, using the energy levels of this as potentials in a problem in which all but one of the remaining coördinates were fixed, and so on. This does not seem to be of apparent practical importance. The second method is to divide the problem, as we have done with helium, into two parts, the valence electron and the rest of the atom. For a complex atom, we first solve, corresponding to (2), a problem in which the coördinates of one electron (corresponding to x_2) are held fast, and all the others are allowed to vary. The potential is then that of the problem in which we have the ion of the atom in question, in the constant external field of a single electron at an arbitrary fixed distance r_2. The energy levels of this problem are functions of the parameter r_2. We then have, corresponding to (3), a problem of the motion of a single electron in a central field. The field is easily seen, by the use of arguments similar to those of the previous section, to be one of the proper nature—reducing to a potential $-e^2/r$ at great distances, and $-Ze_2/r$ + constant, where Z is the charge on the nucleus, for small r. The solution of this is carried out by the method of Fues, just as in helium. Thus we have a general justification of the method of central fields, which has proved so useful empirically, directly from the wave equation. We note the limitation on the accuracy of any such approximation—it cannot give separations between terms of different multiplicities. We must always go to the next approximation to obtain them. It seems doubtful, however, if any unperturbed system could be set up which would not have this difficulty; for the central field theory is the best empirical approximation to the actual facts that has been found and this cannot include the multiplets. The method suggested here, of course, would be extremely difficult to carry out numerically. It justifies us in computing outer orbits from the polarizibility; but as far as inner orbits are concerned, where the problem of the perturbation of the ion in the field of a point charge at finite distances is required, it would become almost impossible. Nevertheless, one should not give up hope. In the meantime, the method could be worked backward, from central fields set up to explain the observed terms, to find empirically the solutions to this perturbation problem.

The method also has important applications to the theory of band spectra, particularly in reference to the vibration of the nuclei. We may divide the variables into two classes: the coördinates of the electrons, and those of the nuclei. Our first problem, corresponding to (2), is one in which the variables representing the nuclei are held fixed. For each electronic stationary state, we then have a function ϵ of the nuclear variables. The next problem, corresponding to (3), is one in which the nuclear variables alone appear, with ϵ acting as a potential energy of interaction between the nuclei. For a diatomic molecule, this is obviously a function only of the distance apart of the nuclei, and this second problem is the

familiar one of the rotating nuclei with a force between them drawing them to a definite distance apart, the force being different for each electronic quantum number. It is easy to see, since the potential V in (2) includes repulsive terms between the nuclei, that $\epsilon_n(x_2)$ must become positively infinite as any two nuclei approach each other. Thus in problem (3) the nuclei will have apparent repulsive forces if they are brought too close together. On the other hand, as the nuclei draw far apart, in many cases the function ϵ_n also increases, giving a position of equilibrium between and possible vibrational stationary states. In other cases there would be no such increase of ϵ_n for increasing r, no finite stationary states are possible, no molecule can form and our problem becomes one of the collision of two atoms. The qualitative side of the application of our method to band spectra has been noticed by Hund;[8] our perturbation method as applied to molecules may be regarded as a mathematical formulation of his ideas on the subject of intermolecular forces.

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*THE ZEEMAN EFFECT OF THE HYPER-FINE STRUCTURE COMPONENTS OF λ 2537 OF MERCURY**

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The hyper-fine structure of λ 2537 of mercury has been shown by Professor R. W. Wood[2] to consist of five lines of very nearly equal intensity. Choosing the central component as the reference line, the separations he reports may be interpreted into relative positions and expressed in milliangstroms as follows: −24, −10, 0, +11, +22.

The optical analysis in the present work was carried out with a Hilger Lummer-Gehrcke plate of crystalline quartz, 4.24 mm. thick, in a manner similar to that employed earlier.[3]

The present observations on the Zeeman effect were made with four different sources of 2537Å radiation, all of which gave mutually consistent

results. The data obtained from over twenty exposures chosen from more than two hundred fifty show that each of the five hyper-fine structure lines has a triplet Zeeman pattern. The results of the work deal with the position and separation of each triplet and the relative intensity of the fine triplets.

In zero magnetic field the positions of the lines, expressed in milli-angstroms, are (taking the central one as the reference), -25.6, -10.3, 00.0, $+11.6$, $+22.1$. In a magnetic field the latter four become triplets with 3/2 the normal separation. There is no Paschen-Back effect evident up to 5800 gausses, the highest field employed, though if there is such an effect it should set in at about 1100 gausses. The parallel components of these four triplets maintain the same relative positions whatever the magnetic field strength. Several special observations were made from which it was established that these components also show no wave-length shift as a group.

The behavior of the hyper-fine structure line at -25.6 is not so simple. The perpendicular components behave as the perpendicular components of a 3/2 normal triplet which starts at -25.6. The parallel component, however, increases in wave-length with increasing field strength. The following equation represents its position in various field strengths:

$$\Delta\lambda = -25.6 + 0.089\sqrt{H}$$

where $\Delta\lambda$ is the position of this component measured from the parallel component of the central reference line, and H is the field strength in gausses.

The estimated relative intensities of the five lines in zero field are, in order of increasing wave-length, 13, 8, 10, 10 and 9. A remarkable change takes place as the field strength is increased. In a field of 5000 gausses it is estimated that the relative intensities of the parallel components (the same holds for the perpendicular components) are 3, 6, 18, 19 and 4. The change in intensity of each component appears to be uniform with the magnetic field strength.

It is very probable that the anomalous behavior of the -25.6 line will, in some way, account for the fact that the polarization of resonance radiation of mercury in zero magnetic field is only 80 per cent instead of 100 per cent as predicted by theory which assumes that the Zeeman pattern of λ 2537 is a 3/2 normal triplet. This belief is supported by recent work of v. Keussler[4] who obtains 100 per cent polarization when the resonance bulb is placed in a magnetic field of 7900 gausses, the lines of force being parallel to the electric vector of the polarized exciting light. The present work shows that in this field the absorption lines of the resonance bulb are at -17.7, -10.3, 00.0, $+11.6$, $+22.1$, while the emission lines of the source are at -25.6 (approximately), -10.3, 00.0, $+11.6$, $+22.1$. Con-

sequently, all the light absorbed in the bulb is contained in the parallel components of the four longer wave-length lines, which are the ones that have 3/2 normal triplet Zeeman patterns. This condition satisfies the requirements of the theory and the results of v. Keussler are in agreement with the prediction.

No doubt in the above case the fact that the intensity of the anomalous line is practically zero plays some part, but if a source giving narrower lines were used, for example, a resonance bulb instead of a water-cooled arc, 100 per cent polarization should be obtained in field strengths as low as 2000 gausses, at which field the intensity of the anomalous line is of considerable magnitude.

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[1] NATIONAL RESEARCH FELLOW.

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THE DIELECTRIC CONSTANT OF ATOMIC HYDROGEN IN UNDULATORY MECHANICS

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1. In a recent paper J. H. Van Vleck[1] used the expressions for the energy of a hydrogen atom in an electric field, derived by I. Waller[2] and the writer,[3] for computing the dielectric constant. The interesting method he applies is analogous to that used by J. H. Jones[4] for the same purpose in Bohr's quantum theory, and is outlined in section 1 of the following paper by Evelyn F. Aylesworth.[5] It appears from this last paper that, in Bohr's theory, the atomic energy has a different expression for weak and for strong fields. If the strength of field is above a certain critical value, the atoms acquire an orientation with respect to it, if it is below this value, their orientation is arbitrary and not affected by the field. The critical value is particularly high for the normal state of the atom, so that here we have the largest deviation from the behavior of the gas in strong fields. On the other hand, Van Vleck shows by a very convincing argument that, from the point of view of undulatory mechanics, an atom in the normal state must change its energy in weak and in strong fields according to the same law.

It seemed, therefore, desirable to treat the problem of the energy change

in an electric field by a different method, in connection with the question of orientation with respect to the field, and to bring out the similarities and the differences between the old and the new theory. The result of this discussion is that, for the excited states of the atom, the conditions are much the same in undulatory mechanics as those found by E. F. Aylesworth; in weak fields the orientation is arbitrary, in strong ones it has a relation to the field. On the other hand, the question of orientation is without meaning for the normal state of the atom, owing to its complete spherical symmetry. For this state, the system can be quantized in any system of polar or parabolic coördinates leading always to the same type of pulsation and to the same energy expression.

2. *Statement of the Mathematical Problem.*—We consider an electron of the charge $-e$ and mass μ moving under the action of a fixed nucleus e and of a superposed homogeneous electric field of the strength D. If x is the coördinate in the direction of the field, the potential energy has the expression $V = e^2/r - eDx$. Though the influence of relativity will be of great importance to us, we may neglect it in this section and write Schroedinger's wave equation in the form

$$\nabla^2\psi + 2\mu(E + e^2/r - eDx)\psi/K^2 = 0. \qquad (1)$$

We are going to express this equation in a system of polar coördinates r, ϑ, φ, and our further treatment of it will be similar to that given for this same case by Schroedinger,[6] however, with one important difference. Schroedinger chose the direction of the field as the polar axis of his system. Now the polar axis is a principal direction of the atom, as it controls the arrangement of the partial oscillations. Its meaning in undulatory dynamics is much the same as in Bohr's theory for a system subject to a complete space quantization in polar coördinates. In our case, choosing the polar axis in the direction of the field would be begging the question we propose to investigate. Our problem is whether there will occur an orientation of the partial oscillations of the atom with respect to the electric field. Therefore, we shall choose the polar axis under an angle γ to the x-direction and shall write for x

$$x = r\cos\vartheta\cos\gamma + r\sin\vartheta\sin\gamma\cos\varphi. \qquad (2)$$

For solving equation (1) we use the standard method of successive approximations, putting

$$\begin{cases} E = E_0 + E_1D + E_2D^2, \\ \psi = \psi_0 + \psi_1D + \psi_2D^2. \end{cases} \qquad (3)$$

Substituting into (1) and collecting terms of equal order of magnitude

$$\begin{aligned} K^2\nabla^2\psi_0/2\mu + (E_0 + e^2/r)\psi_0 &= 0, \\ K^2\nabla^2\psi_1/2\mu + (E_0 + e^2/r)\psi_1 &= (ex - E_1)\psi_0, \\ K^2\nabla^2\psi_2/2\mu + (E_0 + e^2r/)\psi_2 &= (ex - E_1)\psi_1 - E_2\psi_0. \end{aligned} \qquad (4)$$

As in previous papers, we use the abbreviations

$$\alpha^2 = -2\mu E_0/K^2, \qquad l = \mu e^2/K^2\alpha, \tag{5}$$

and, moreover, we introduce a new dependent variable by the substitution

$$\psi = e^{\alpha r}\Phi. \tag{6}$$

Equation (4) assumes the form

$$\begin{aligned}
&\nabla^2\Phi_0 + 2\alpha\partial\Phi_0/\partial r - 2\alpha(l-1)\Phi_0/r = 0,\\
&\nabla^2\Phi_1 + 2\alpha\partial\Phi_1/\partial r - 2\alpha(l-1)\Phi_1/r = 2\mu(ex - E_1)\Phi_0/K^2,\\
&\nabla^2\Phi_2 + 2\alpha\partial\Phi_2/\partial r - 2\alpha(l-1)\Phi_2/r = 2\mu[(ex - E_1)\Phi_1 - E_2\Phi_2]/K^2.
\end{aligned} \tag{7}$$

In order to treat these equations mathematically, we use the artifice of generalizing them and solving them for any value of α and for an integral value of l. After such a solution is found, we can specialize it by reintroducing relation (5) between α and l. Only solutions satisfying Schroedinger's conditions of finiteness will be considered.

3. *Auxiliary Formulae.*—The first of the equations (7) represents the wave motion in the atom not subjected to an external field. This problem has been exhaustively treated by Schroedinger and its solution is known to be

$$A_{nm}N(l,n)P_n^m(\cos\vartheta)\begin{matrix}\cos\\ \sin\end{matrix} m\varphi. \tag{8}$$

A_{nm} is a constant, $P_n^m(\cos\vartheta)$ the associated spherical harmonic, and $N(l, n)$ is related to the functions χ and M, defined in one of our previous papers,[7] in the following way

$$N(l, n) = e^{-\alpha r}\chi(l, n) = r^n M(l, n). \tag{9}$$

Accordingly, this function satisfies the equation

$$\frac{d^2N}{dr^2} + 2\left(\alpha + \frac{1}{r}\right)\frac{dN}{dr} - \left[\frac{2\alpha(l-1)}{r} + \frac{n(n+1)}{r^2}\right]N = 0. \tag{10}$$

The integers n, m can have any value consistent with the inequality $m \leq n \leq l-1$.

Let us now consider the inhomogeneous equation

$$\nabla^2 u + 2\alpha\partial u/\partial r - 2\alpha(l-1)u/r = AN(l', n)P_n^m\cos m\varphi/r. \tag{11}$$

A solution of it is

$$u = \frac{A}{2\alpha(l'-l)}N(l', n)P_n^m\cos m\varphi, \tag{12}$$

provided that $l' \neq l$. If $l' = l$, there is no solution satisfying the requirements of finiteness.

In order to apply this result to equations (7), we shall have to reduce

the right sides. From formulae (8), (9), (10) of paper,[7] we easily deduce the following relations:

$$\begin{aligned} 2\alpha r N(l,n) &= (l+n+1)N(l+1,n) - 2lN(l,n) + (l-n-1)N(l-1,n) \\ &= \frac{2n(2n+1)}{2\alpha}\,[N(l+1,n-1) - 2N(l,n-1) + N(l-1,n-1)] \\ &= \frac{2\alpha}{(2n+2)(2n+3)}\,[(l+n+1)(l+n+2)N(l+1,n+1) - \\ &\quad - 2(l+n+1)(l-n-1)N(l,n+1) + (l-n-1)(l-n-2)N(l-1,n+1)]. \end{aligned} \tag{13}$$

The parameter α is supposed to be the same in all the terms of these relations. In addition to these formulae, we shall have to use the well-known relations of the theory of spherical harmonics

$$(2n+1)\cos\vartheta P_n^m = (n-m+1)P_{n+1}^m + (n+m)P_{n-1}^m, \tag{14}$$

$$\begin{aligned} (2n+1)\sin\vartheta\, P_n^m &= -(n-m+1)(n-m)P_{n+1}^{m-1} \\ &\quad + (n+m-1)(n+m)P_{n-1}^{m-1} = P_{n+1}^{m+1} - P_{n-1}^{m+1}. \end{aligned}$$

4. *Conditions in Strong Fields.*—If the field is so strong that the relativistic correction term is negligible compared with the electric, the equations of section 2 are strictly applicable. The general solution of the first equation (7) can be written in the form

$$\Phi_0 = \sum_{n,m} A_{nm} N(l,n) P_n^m(\cos\vartheta)\cos m\varphi, \tag{15}$$

(if we omit for short the terms with $\sin m\varphi$). To obtain Φ_1, we have to represent the right side of the second equation as a sum of terms of the type (11). This can be easily done by means of relations (13) and (14). The terms of this expansion, proportional to one of the products of the sum (15), would prevent Φ_1 from satisfying Schroedinger's conditions of finiteness. We must, therefore, choose the value of E_1, in such a way as to make these terms vanish.

It will be sufficient to carry this through for the simple case $l = 2$, as all conclusions will be applicable to the general case. If $l = 2$,

$$\Phi_0 = A_{11}N(2,1)P_1^1(\cos\vartheta)\cos\varphi + A_{10}N(2,0)P_1(\cos\vartheta) + A_{00}N(1,0)P_0. \tag{16}$$

The terms of $\alpha r(ex - E_1)\Phi_0$, proportional to these, are

$$\begin{aligned} &(2A_{11}E_1 + 3A_{00}\sin\gamma)N(2,1)P_1^1\cos\varphi + (2A_{10}E_1 + 3A_{00}\cos\gamma)N(2,0)P_1 \\ &\quad + [2A_{00}E_1 + 3(A_{10}\cos\gamma + A_{11}\sin\gamma)/\alpha^2]N(2,0)P_0. \end{aligned}$$

This leads to the three conditions

$$\begin{aligned} 2A_{11}E_1 + 3A_{00}\sin\gamma = 0, \qquad 2A_{10}E_1 + 3A_{00}\cos\gamma = 0, \\ 2\alpha^2 A_{00}E_1 + 3(A_{10}\cos\gamma + A_{11}\sin\gamma) = 0. \end{aligned} \tag{17}$$

Corresponding to the three partial oscillations, we have to expect three values of E_1. The quantization coördinates are chosen in the right way, when each of these three values can be associated with one of the three possible combination of quantic numbers n, m:(1, 1), (1, 0), (0, 0). However, our purpose is to answer the simpler question, whether it is permissible to choose the axis of the system in the arbitrary direction we have given it. Since φ is the azimuth around the axis, the quantic number referring to the axis is m. The axis is chosen in a correct way, if we can associate one value of E_1, with $m = 1$, and two with $m = 0$. Tested by this criterion, our axis is not well chosen, as our equations (17) are mixed with respect to the second indices of A_{nm}. If we try to remedy this situation by a linear substitution, the only substitution that can be found is

$$A_{11} = B_{10} \sin \gamma + B_{11} \cos \gamma, \qquad A_{10} = B_{10} \cos \gamma - B_{11} \sin \gamma, \qquad A_{00} = B_{00}, \tag{18}$$

which brings equations (17) into the form

$$2\alpha^2 B_{00} E_1 + 3B_{10} = 0, \qquad 3B_{00} + 3B_{10} E_1 = 0, \qquad B_{11} E_1 = 0. \tag{19}$$

The coördinates corresponding to the coefficients B_{nm} satisfy our requirements. The geometrical meaning of this transformation becomes apparent, when we substitute (18) into expression (15) for Φ_0. Denoting by ϑ', φ' the polar angle and azimuth referred to the direction x and the x, y plane, we obtain, with the aid of well-known trigonometrical relations,

$$\Phi_0 = B_{11} N(2, 1) P_1^1(\cos \vartheta') \cos \varphi' + B_{10} N(2, 1) P_1(\cos \vartheta') + B_{00} N(2, 0) P_0.$$

Our substitution (18) represents, therefore, a rotation of the polar axis into the direction x. In other words, the axis of the atom has the direction of the electric field.

5. *Conditions in Weak Fields.*—If the relativistic term is more important than the electric, we have to take it into account first. The motion without electric field is then the relativistic motion, and, instead of the first equation (7), we should take the equation corresponding to this case. The main feature of the relativistic motion is that in it the characteristic value E_0 is a function, not only of the quantic number l, but also of n. This is, in fact, the only point of any importance for our purpose: if we bear it in mind, we may neglect relativity in every other respect and use the same analysis as in the previous case. Instead of (15), we shall have for the total quantic number $l = 2$ two possible expressions of Φ_0, corresponding to $n = 1$ and $n = 0$,

$$\Phi_0^{(1)} = A_{11}N(2, 1)P_1^1 \cos\varphi + A_{10}N(2, 1)P_1,$$
$$\Phi_0^{(0)} = A_{00}N(2, 0)P_0. \tag{20}$$

Therefore, the equations analogous to (17) will be

$$A_{11}E_1 = 0, \qquad A_{10}E_1 = 0, \qquad A_{00}E_1 = 0. \tag{21}$$

We see that the requirement discussed in last section is satisfied: we can associate one of the three values of E_1 with each of the existing combinations nm. (Incidentally $E_1 = 0$, in every case.) This shows that our system of polar coördinates with an arbitrary orientation of the axis is an adequate system for the quantization or, in other words, the atomic axis may have any direction.

Whether a given field is to be considered as strong or weak depends on the ratio of the corresponding electric perturbation to the relativistic. As the expressions for the relativistic doublet and for the Stark effect are almost the same in the old and the new theory, we have, roughly speaking, the same criterion in both of them.[5]

6. *Normal State of the Atom.*—In the normal state $l = 1$, $n = m = 0$. The solution of the unperturbed motion is

$$\Phi_0 = A_{00}N(1, 0)P_0. \tag{22}$$

By the same method as in section (4) we find for E_1 the condition $A_{00}E_1 = 0$. There is only one value of E_1 and one combination of the quantic numbers: (0, 0). The requirement of section 4 is, therefore, always satisfied. For strong, as for weak fields, we can choose any system of polar coördinates as the coördinates of quantization. We obtain for Φ_1

$$\Phi_1 = \mu A_{00}[N(3, 1) - 2N(2, 1)](P_1 \cos\gamma + P_1^1 \cos\varphi \sin\gamma)/K^2\alpha^2. \tag{23}$$

Substituting this into the third equation (7) we can compute the part of the right side which is proportional to $N(1, 0)P_0$ and must vanish:

$$A(9\mu/2K^2\alpha^4 + 2E_2)N(1, 0)P_0. \tag{24}$$

The angle γ has dropped out of this expression and it gives always the same value for the coefficient:

$$E_2 = -9K^6/4\mu^3e^6, \tag{25}$$

which is, moreover, identical with the value resulting for the normal state in our theory of the Stark effect.

The physical cause of this particularity of the normal state becomes apparent if we notice that $N(1, 0) = P_0 = 1$. Therefore, $\Phi_0 = A_{00} =$ const., and the amplitude ψ of the oscillation becomes, according to equation (6), $\psi = A_{00} \exp(\alpha r)$. The normal state represents a radial pulsation of complete central symmetry. It is the same in every system of co-

ordinates and, therefore, is always affected in the same way by an electric field. If we describe the atom by parabolical coördinates,[3] we get for the normal state $\psi = A_{00} \exp[\alpha(\xi + \eta)/2]$, where $(\xi + \eta)/2 = r$, so that here again we get the same radial pulsation.

The numerical value of E_2, according to formula (25), is $E_2 = -3{,}29.10^{-25}$ cm.[3] The dielectric constant[1] is connected with E_2 by the relation $\epsilon - 1 = 8\pi N E_2$ (N, number of atoms in unit volume), leading to the value $\epsilon - 1 = 0{,}000224$.

The spin of the electron has not been considered in this theory, but it hardly can introduce any appreciable change. We completely agree with Van Vleck's opinion that this theoretical value is more reliable than the result of the extremely difficult experimental determination of the index of refraction. The fact that for helium the experimental value $\epsilon - 1 = 0{,}000074$ is very different from the above value, is not consistent with a model in which one electron is close to the nucleus, the other farther away. It can be regarded as a further confirmation of Heisenberg's theory assuming equivalent orbits for the two electrons.

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THE DIELECTRIC CONSTANT OF ATOMIC HYDROGEN FROM THE POINT OF VIEW OF BOHR'S QUANTUM THEORY

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1. The following lines represent an abridgment of my thesis presented a year ago to the University of California. Their main purport is in relation to the question *whether a hydrogen atom in an electric field acquires a definite orientation or not*, and this question is answered from the point of view of Bohr's theory. Since this investigation was begun, the quantum theory has undergone a rapid development owing to the brilliant work of Heisenberg, Born, Schroedinger and others. The numerical part of our work is superseded by this new point of view, but our general results and the whole approach of the problem remain of practical value even in the new quantum theory, as will appear from the preceding paper by Professor

P. S. Epstein. Accordingly, we present in the following sections the general lines of our reasoning, suppressing the details of calculation.

The problem of the dielectric constant of atomic hydrogen was treated a few years ago by J. H. Jones.[1] Let the expression of the energy which a hydrogen atom assumes in an electric field of the strength F be to terms of the second order

$$E = E_0 + E_1F + E_2F^2. \tag{1}$$

The coefficients E_1 and E_2 were known from Epstein's work on the Stark effect.[2] In the normal state of the atom, in particular, $E_1 = 0$ and $E_2 = h^6/2(2\pi e)^6\mu^3$, where h is Planck's constant of action, e and μ the charge and mass of the electron. It can readily be shown that the dielectric constant must satisfy the relation

$$K - 1 = -8\pi NE_2, \tag{2}$$

N being the number of atoms in unit volume of the gas. Substituting the above value of E_2, Jones obtains

$$K - 1 = 4\pi Nh^6/(2\pi e)^6\mu^3. \tag{3}$$

This formula is, however, in contradiction with the results which one gets from the extrapolation of the refractive index n, for frequencies ν approaching zero.[3] Substituting $\nu = 0$ into the formula derived for n^2 from Bohr's quantum theory, we have

$$n^2 - 1 = 11Nh^6/64\pi^6e^6\mu^3. \tag{4}$$

It is true that the foundations of the older quantum theory, on which this formula is based, were unreliable and have since been changed. It has, however, been pointed out by several physicists that the dispersion theory in question must lead to correct results for low frequencies.

The purpose of the present communication is to resolve this contradiction. From the analogy with Kramers'[4] work on the Stark effect, it seemed probable that the discrepancy was due to the omission on Jones' part of considering the relativity terms in the motion of the electron. For this reason the problem was studied in its completeness, taking into account the effect produced by the relativistic change of mass, as well as the effect due to the presence of the electric field.

2. We consider an electron, moving with the velocity v ($= \beta c$, where c is the velocity of light) around a fixed center having the charge e. The whole system is placed in a homogeneous electric field of the strength F. We choose the direction of F as the z-axis of a Cartesian system x, y, z; and, in addition to the Cartesian system, we will make use of a system of polar coördinates given by the relations.

$$x = r \sin\vartheta \cos\varphi, \qquad y = r \sin\vartheta \sin\varphi, \qquad z = r \cos\vartheta.$$

The total energy or Hamiltonian function can be written in the form

$$H = T - e^2/r - eFz, \tag{5}$$

where T is the relativistic expression for the kinetic energy

$$T = \mu c^2[1/\sqrt{1-\beta^2} - 1] = \mu v^2/2 + 3\mu v^4/8c^2 + \ldots$$

Therefore,

$$H = H_1 + 3\mu v^4/8c^2 - eFz, \tag{6}$$

where

$$H_1 = \mu v^2/2 - e^2/r \tag{7}$$

is the Hamiltonian function of the unperturbed or first intermediate motion, $3\mu v^4/8c^2$ is the *relativistic*, and $-eFz$ the *electric perturbation term*. H_1 defines the simple Kepler motion whose integral is well known. We shall require the angular variables and corresponding momenta in this motion and may refer in this respect to the formulae collected in a paper of Epstein's.[3] Instead of Epstein's variables u, w, it will be more convenient to use a new set of canonical coördinates p, q, resulting from the former by the contact transformation

$$\begin{aligned} q_1 &= w_1 - w_2, & q_2 &= w_2 - w_3, & q_3 &= w_3 \\ p_1 &= u_1, & p_2 &= u_1 + u_2, & p_3 &= u_1 + u_2 + u_3. \end{aligned}$$

The physical meaning of these coördinates is as follows: p_3 is connected with the energy of the motion by the relation

$$H_1 = \mu e^4/2p_3^2. \tag{8}$$

p_2 represents the principal moment of momentum and p_1 its projection on the z-axis. If ϵ is the eccentricity of the orbit and λ the angle between the normal to the orbit and the z-axis:

$$\sqrt{1-\epsilon^2} = p_2/p_3, \qquad \cos\lambda = p_1/p_2. \tag{9}$$

From the expression (8) for H_1 there follows, by means of the Hamiltonian equations, $\dot{q}_1 = \dot{q}_2 = 0$, $\dot{q}_3 = \text{const}$. The coördinates q_1 and q_2, therefore, remain constant, while q_3 is a linear function of the time t.

The general rule for the quantization of degenerate systems of this type is that only the momentum on which H_1 depends must be quantized. There is, therefore, only one quantum condition imposed on the system, namely,

$$p_3 = n_3 h/2\pi. \tag{10}$$

That means that our orbit has a constant energy and a constant major

axis (since the energy is uniquely determined by the major axis), but any arbitrary eccentricity and orientation.

We are now going to consider the change of this motion produced by the presence of the relativistic and electric terms, by means of the theory of perturbations. We will use this theory in the form developed by Epstein[5] (especially in section 10 of his paper), which requires an expansion of the perturbation terms in a trigonometric series. The trigonometric functions have the arguments $\tau_1 q_1 + \tau_2 q_2 + \tau_3 q_3$ (τ being integers), and we shall concentrate our attention on the so-called *degenerate* terms of this series. The degenerate terms are those which do not contain in their arguments the variables q conjugate to any of the momenta on which the Hamiltonian function depends. In our case the function H_1 depends only on p_3, so that the degenerate terms are those which are independent of q_3. Transforming the electric perturbation term by means of the above-mentioned formulae, we see that it contains only one single degenerate term.

$$R = -\frac{3F}{2\mu e}\frac{p_2}{p_2}\sqrt{p_3^2 - p_2^2}\cdot\sqrt{p_2^2 - p_1^2}\cos q_2. \qquad (11)$$

It is shown in the general theory that only the degenerate terms can lead to material change of the conditions of quantization. As the arguments of these terms are constant, while the arguments of the rest of the expansion are linear functions of time, the totality of the degenerate terms is the time average of the perturbation function taken over a long time. In this form the definition of the degenerate part of the perturbation function was given by Bohr.[6]

3. *Conditions in Strong Fields.*—It will be necessary to discuss this case, though only our method of approach is new, while the results were known from Bohr's[6] and Kramers'[4] work. If the electric perturbation dominates over the relativistic, our process of successive approximations must start from considering the electric terms. As we have pointed out, the most important one among them is the degenerate term (11). Our second step will be, therefore, the consideration of the Hamiltonian equation

$$H_2 = H_1 + R = \text{const.}, \qquad (12)$$

where H_1 and R are given by equation (8) and (11). This function is independent of q_1 and q_3, and, therefore, p_1 and p_3 will be constant. Accordingly, p_2 will be a function of q_2 alone, the functional relationship being given by (12). Since H_1 is constant, we can throw H_1 into the constant writing the equation

$$R = 3Fp_3\Delta/2\mu e, \qquad (13)$$

where Δ is the new constant.

We have now to find the angular coördinates p', q' for this motion. According to the general rules, the angle momenta are given by

$$p_1' = p_1, \qquad p_2' = \frac{1}{2\pi} \oint p_2 dq_2, \qquad p_3' = p_3.$$

p_2 depends on q_2 and Δ, and the second equation can be regarded as a relation determining Δ. Carrying out the integration, we find

$$\Delta = 2p_2' - p_1' + p_3'. \tag{14}$$

In addition to this, from the real character of the function p_2, there follows the restriction

$$| \Delta | \leq p_3' - p_1'. \tag{15}$$

The Hamiltonian function becomes

$$H_2 = \mu e^4/2p_3'^2 - p_3'\Delta \cdot 3F/2\mu e. \tag{16}$$

Instead of p_2', we can as well introduce as one of the angle momenta the linear expression Δ. From the principle mentioned in section 2, that the momenta entering into the expression of the Hamiltonian function are subject to quantization, we conclude that we have to add to condition (10) a second quantum relation

$$\Delta = nh/2\pi. \tag{17}$$

This condition combined with the restriction (15) makes our term $p_3'\Delta \cdot 3F/2\mu e$ completely equivalent to Epstein's expression of the first order Stark effect,[2] leading to exactly the same energy levels.

The geometrical significance of relation (17) amounts to a restriction imposed on the possible orientations of the orbit. It will be enough to discuss this for the normal state of the atom, in which we are most interested in connection with the dielectric constant. In the normal state $p_3 = 1$. From (15) we see that Δ can assume the values $\pm h/2\pi$ and 0. However, the cases $\pm h/2\pi$ must be ruled out, since they lead to $p_1 = 0$ and $p_2 = 0$, representing orbits that would go through the nucleus. There remains $\Delta = 0$. From (11) and (12) we see that this can be satisfied either by putting $p_1 = p_2$ or $p_2 = p_3$. The analysis of the second assumption shows, however, that it is possible only when $p_1 = p_3$, so that in every case we have $p_1 = p_2$, or from (9) $\cos \lambda = 0$, $\lambda = \pm \pi/2$. In the unperturbed motion p_1 and p_2 are completely arbitrary, so that the angle λ between the normal to the orbit and the z-axis can assume any value. If we superpose a strong electric field, the normal can be only parallel or antiparallel to the direction of the field (z-axis). On the other hand, p_2 is not restricted by any condition, so that the orbit can have any eccentricity.

Our new coördinates q_1', q_2', q_3', though dependent on the direction of the electric field, will not yet quite correspond to the parabolic coördinates used in the usual theory of the Stark effect. In order to obtain these, it would be necessary to go further in the approximation, by supposing that even the second order terms of the electric perturbation dominate over the relativistic terms.

4. *Conditions in Weak Fields.*—When the field is so weak that the relativistic perturbation term dominates over the electric, the effect of relativity must be taken into account first. It is not necessary to discuss the mathematical side of this step, since the effect of relativity is fully known from the work of Sommerfeld.[7] We use the same variables as in the unperturbed motion, but the choice of the momentum p_2, is now restricted by an additional quantum condition introduced by the relativistic term: $p_2 = n_2 h/2\pi$, while p_1 remains arbitrary. Together with (10), this condition means that both the major axis and the eccentricity of the orbit are restricted by quantum conditions, while its orientation is arbitrary. The Hamiltonian function of the system is according to Sommerfeld

$$H_2' = -\mu e^4/2p_3^2 - \mu e^8(p_3/p_2 - 3/4)/2c^2p_3^2. \qquad (18)$$

If we wish to go a step farther, and to study the change of this motion produced by the electric field, we have to proceed exactly as in section 3. Again we may expect a material change of coördinates only for the degenerate terms, which in this case will depend only on the variable q_1. However, we have pointed out that all the terms of the expansion of the electric perturbation depend either on q_3 or on q_2. *From our new point of view there will be no degenerate terms at all.* This means that our system of polar coördinates will remain the adequate system for quantization even if we take into account the electric perturbation.

This result is of extreme importance for the theory of the dielectric constant. In the case of a very strong field the parabolical coördinates of the Stark effect must be used, giving Epstein's expressions for the atomic energy. Since Jones' theory is based on these expressions, the value of the dielectric constant obtained by him applies only to this case. The conditions in weak fields differ from those assumed in Jones' theory in two respects. In the first place, *the computation must be carried out in polar coördinates*, and this leads to an expression of the energy different from that obtained by Epstein. In the second place, *the orientation of the polar axis* with respect to the electric field *is arbitrary*, so that the energy will depend on this orientation. In order to arrive at an expression of the dielectric constant we will have to compute the statistical average of the energy for a large number of atoms, each of which is oriented in a different way.

For the reasons mentioned in section 1, we shall not enter here into the details of this calculation (though they represented a large part of our thesis). We simply give the result

$$\epsilon - 1 = 11Nh^6/64\pi^6e^6\mu^3. \tag{19}$$

We see that this expression is identical with formula (4) for the limiting value of the index of refraction, so that the discrepancy between the theoretical values of these two quantities is removed.

5. It is still necessary to discuss what we have to regard as a weak field in the sense of this theory. In a rough way we have said: the strength of field F must be such that the electric term becomes less important than the relativistic. We obtain a more accurate estimate from Bohr's view of the degenerate terms as the time average of the perturbation. From this point of view the reason why the term (11) is degenerate in strong fields, and not degenerate in weak ones, is that q_2 is a constant in the first case and a linear function of the time in the second. A proper measure of the degree of degeneration is, therefore, given by the rate of change $\dot{q}_2$. This rate of change follows by means of $\dot{q}_2 = \partial H/\partial p_2$ from expression (18) as $\mu e^8/2c^2p_3^3p_2^2$. In a similar way, if we take into account first the electric term, the degree of degeneration of the relativistic term will depend on the rate of change obtained from (16), $\partial H_2/\partial\Delta = 3Fp_3/2\mu e$. The critical value of the electric field will be determined by the equality in absolute value of the two expressions: $F = \mu^2e^9/3c^2p_3^4p_2^2$. If we substitute for p_2, p_3 the corresponding quantic numbers: $F = \mu^2e^9(2\pi)^6/3c^2h^6n_3^4n_2^2$. Substituting the numerical values of the constants

$$F = (93{,}000/n_3^4n_2^2)\text{volt/cm}. \tag{20}$$

Fields small compared with this value must be considered weak. In the normal state of the atom ($n_2 = n_3 = 1$) the critical value is 93,000 volt/cm., so that the fields used in the experimental determination of the dielectric constant must certainly be regarded as weak. The critical value rapidly decreases as we go over to higher excited states.

As a brief summary we may say; the orbits of the hydrogen atom will acquire an orientation with respect to an external electric field only if the strength of field is above the critical value (20). There will be no orientation for fields considerably lower than this value. The fields used in the measurement of the dielectric constant must be considered as low, and formula (19) must be used.

It gives me pleasure to acknowledge my indebtedness to Professor Paul S. Epstein of the California Institute of Technology, for suggesting this investigation, and to Professor W. H. Williams of the University of California, for his assistance in carrying it out.

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DIRECT AND INDIRECT PRODUCTION OF CHARACTERISTIC X-RAYS

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I. *The Problem.*—When electrons are ejected from the K orbits of atoms in the target of an X-ray tube, the question arises: Are most of them ejected by direct action of the cathode rays through their repulsive forces; or are they ejected by an indirect process, the photoelectric effect of continuous-spectrum X-rays excited by the cathode rays; or perhaps, do both processes occur often? From the experimental standpoint, this question takes the form: Are the characteristic rays from the target of a tube mostly "direct primary rays," or are they mostly "indirect primary rays" (really a restricted class of secondary rays), or are they a mixture of comparable amounts of both classes?

Beatty,[1] in 1912, said they were mostly direct and presented such clear experimental evidence that his answer was accepted for many years as conclusive. In 1926, however Balderston,[2] by calculations from data of wholly different types, came to exactly the reverse conclusion. Evidently, the question calls for further investigation.

II. *Emergence-Angle Experiments.*—Two methods were used in the present work, both based on the fact that such indirect rays as may exist are produced at a variety of depths averaging somewhat greater than the mean depth of production of rays in the continuous spectrum. This is obvious qualitatively from the fact that, in any fairly heavy element, X-rays of the types needed for fluorescence of its K series are more penetrating than the cathode rays producing them.

If, therefore, any means can be found for revealing differences in the depths of production of X-rays, of these two classes, the question at hand can be answered. The first of the two methods was an adaptation of Ham's[3] experiment on total, or unresolved, X-rays, applied here to the

rays as resolved by the spectrometer. The underlying principle is that if the rays from any atom are emitted with equal intensities in all directions, then the deeper the atom is within the target, the more effect the absorption by the target material will have in causing differences of intensity between rays emerging from its surface nearly perpendicularly or at small angles.

In the present case, the target was a layer of silver, 25 microns thick, electroplated upon copper. When it was bombarded by cathode rays driven by a steady voltage of 35 kv., d. c., the continuous-spectrum rays were produced, as will be shown below, at mean depths of less than a micron, while the indirect characteristic rays came from depths averaging several microns. The difference between these depths is such as to cause considerable changes in the ratio of indirect characteristic rays to continuous-spectrum rays of the same wave-length, when the emergence angle ϵ, between the target surface and the rays to the spectrometer, is reduced below 20°.

For quantitative calculation, this ratio must be defined more specifically in terms of spectrum graphs in which electrometer readings are plotted against glancing angles. As the tube is turned to reduce the angle of emergence, the change in apparent size of the focal spot, as seen from the spectrometer crystal, causes a change in the resolving power of the spectrometer. A simple ratio of the maximum ordinate of the Kα peak to that of the continuous spectrum under it would, therefore, be misleading, and the only true basis for comparison is the ratio of the *area*, A, of the Kα peak, to the *ordinate*, C, of the continuous spectrum in its neighborhood. This ratio, which is of the dimensions of an interval of glancing angles, gives the width of a block of continuous spectrum carrying the same total energy as the α lines.

The next problem is to calculate this ratio, assuming all the line radiation to be indirect. For this purpose the following assumptions, definitions and data were adopted, and will prove useful in the theory of the second method:

(1) The continuous spectrum, as emitted from any atom, is of the same form and intensity in all directions.

(2) Continuous-spectrum rays of the α-line frequency emerging from the target are reduced by absorption to a fraction, $\exp\{-\mu_\alpha \bar{x}_\alpha \csc \epsilon\}$ where μ_α is their absorption coefficient and $\bar{x}_\alpha$ their mean depth of production.

(3) The mean depth of production for rays of any frequency may be found by the method of Webster and Hennings,[4] depending on the extent to which the K-absorption limit of the target material affects the observed emission spectrum.

(4) Mean depths as thus found for the present case are small enough

so that for calculation of the indirect radiation one may treat the continuous-spectrum rays as if they all originated at the surface.

(5) The absorption coefficient μ at any frequency above the K limit is $\mu_\alpha R_L^K \eta^{-3}$, where $\eta = \frac{\nu}{\nu_\alpha}$ and R_L^K is the absorption limit ratio, given by Richtmyer[5] for silver as 7.8; in calculations on the second (more accurate) method, this assumption is replaced by Richtmyer's more accurate formula for μ.

(6) The number of α-line quanta emitted indirectly is a constant fraction, u_α, of the number of absorbed quanta of frequency greater than the K-limit frequency ν_K, and u_α is as given by Balderston[2] for silver, $\frac{5}{6} \times 0.75$, or 0.625.

(7) The total intensity of the α-line rays, or energy leaving the target per unit time and per unit solid angle in the direction ϵ, is E_α, and is made up of two parts, direct and indirect, called E'_α and E''_α, respectively.

(8) The observed α peak has an area $A = A' + A''$, likewise determined by the equation $A = SE_\alpha$, where S is the over-all sensitivity of the spectrometer and its accessories.

(9) The continuous spectrum has its true intensity per unit frequency interval $I(V, \nu)$, and they are related through the formula

$$S = \frac{C\,d\,\theta}{I(V, \nu)d\nu} = \frac{C \tan \theta}{\nu I(V, \nu)}$$

where θ is the glancing angle for the frequency ν.

(10) For a single element,

$$I(V, \nu) = K\{(\nu_0 - \nu) + B\nu_\alpha\}$$

where K is a constant and $h\nu_0 = eV$; the term $B\nu_\alpha$ is expressed as a multiple of ν_α merely for convenience in integration, and is treated as if it were constant with $B = 0.10$, this value being a rough estimate from Webster and Hennings'[6] data on Mo.

With these assumptions and definitions, it is a simple matter to set up the integral,

$$E''_\alpha = \frac{1}{2} \int_{\nu_K}^{\nu_0} \int_0^{\pi/2} \int_0^{\infty} u_\alpha \frac{\nu_\alpha}{\nu} \mu I(V, \nu) \exp\left\{-\mu r - \mu_\alpha r \cos\psi \sin\epsilon\right\} \sin\psi dr d\psi d\nu,$$

where ψ is the colatitude in a spherical coördinate system.

This integrates readily as far as

$$E''_\alpha = \frac{1}{2} u_\alpha \int_{\nu_K}^{\nu_0} \frac{\nu_\alpha}{\nu} \frac{\mu}{\mu_\alpha \csc\epsilon} I(V, \nu) \log\left(1 + \frac{\mu_\alpha \csc\epsilon}{\mu}\right) d\nu,$$

from which,

$$\frac{A''}{C} = \frac{\frac{1}{2}u_\alpha R_L^K \tan\theta \sin\epsilon}{(\eta_0 - 1 + B)\exp\left\{-\mu_\alpha \bar{x}_\alpha \csc\epsilon\right\}} \int_{\eta_K}^{\eta_0} \frac{\eta_0 - \eta + B}{\eta^4} \log\left(1 + \eta^3 \frac{\csc\epsilon}{R_L^K}\right) d\eta,$$

where $\eta_0 = \frac{\nu_0}{\nu_\alpha}$ and $\eta_K = \frac{\nu_K}{\nu_\alpha}$.

Evaluating this graphically for silver at 35 kv., the results are as follows:

$$\epsilon = 20^\circ\ ,\ 5^\circ\ ,\ 1^\circ\ ;$$
$$\frac{A''}{C} = 11.9',\ 7.4',\ 4.0'.$$

The observed values of the area-to-ordinate ratios for these angles are obtained from figure 1, as

$$\epsilon = 20^\circ\ ,\ 5^\circ\ ,\ <1^\circ;$$
$$\frac{A}{C} = 32.4',\ 30.7',\ 36'.$$

In the absolute magnitude of the values calculated for A''/C, there are great opportunities for error, due to errors in the numerous assumptions listed above. Slight changes in them result in changes in A''/C much greater than one might expect; thus a moderate displacement of the center of gravity of the spectrum toward shorter wave-lengths, combined with a moderate asymmetry in space, can give calculated values of A''/C actually greater than the observed A/C. In Balderston's paper, quoted above,[2] the only means at hand for an estimate of A''/A was a comparison of quantities essentially equivalent to the present A''/C and A/C, for a single value of ϵ. It seems probable, therefore, that some difference in assumptions about the continuous spectrum explains the difference between his conclusions about A''/A and those to be drawn from the values given above.

However unreliable the present calculated values of A''/C may be, nevertheless the calculated changes of A''/C with ϵ are on a much firmer basis. Even if, by any reasonable changes of assumptions, the calculated A''/C at 20° were made to agree with A/C, the drops in A''/C to about 2/3 and 1/3 of the 20° value would still occur nearly as before. The conclusions from these experiments must, therefore, rest primarily on a comparison of A/C and A''/C with regard to their changes.

Returning to the hypothesis that the true A''/C is as calculated, and assuming the rest of the observed peak A to be made up of direct radiation A', with A'/C the same at all angles, the decrease in A/C in reducing ϵ from 20° to 5° is of the calculated order of magnitude.

The rise in A/C in reducing ϵ still further, from 5° to below 1°, was at the time of the experiments a phenomenon quite unexpected. It may be

nothing but experimental error, since the rays below 1° were very weak, but if it is real an explanation may be found in considering the probable changes in A'/C. Direct line-spectrum rays, as one may show by a thin-target analysis,[6] should be produced at a mean depth slightly less than that of the continuous spectrum. Both these depths being small compared to

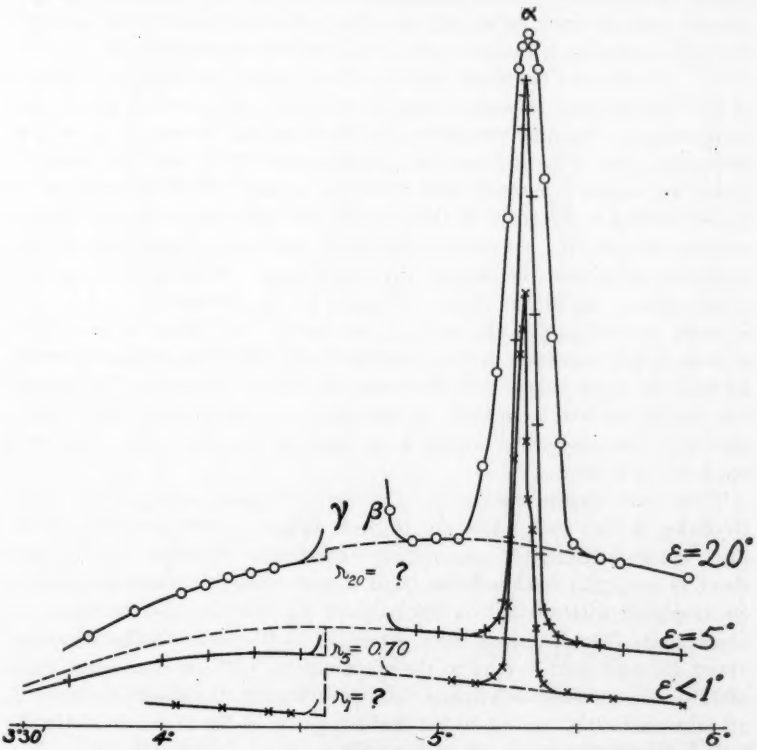

FIGURE 1

Spectra of silver at 35 kv. The scales of these spectra differ, because of differences in slit widths and times of exposure of the ionization chamber to the rays. The depth of production of rays of the continuous spectrum was estimated from the ratio r at $\epsilon = 5°$, as 0.5 micron. The value of r at 20° was too near unity to give a reliable estimate, and its value at 1° too uncertain because of faintness of the rays, but so far as they go, the 20° and 1° ratios are consistent with the above depth.

that of the indirect rays, the effect of the direct rays on A/C should become evident only at emergence angles below a degree or two. There, however, where most of the indirect rays are eliminated by absorption, it should cause an effect of the sort observed.

These minor changes in A/C, while consistent enough with the theory, must nevertheless be regarded as unreliable evidence, because they are only of the order of magnitude of the limits of probable error. The more important result is that A/C shows no such large and systematic decrease as would be expected if the line-spectrum rays were nearly all of indirect origin. From that fact it seems reasonable to conclude that for the present case at least (silver at 1.4 times its excitation voltage) a large fraction, probably a majority, of the K-series rays are direct.

III. *Block-and-Film Experiments.*—For a more quantitative estimate of the ratio of direct to indirect rays, in relation to which the above experiments may be regarded primarily as a check against serious errors or misinterpretations, a second method of separating these rays was devised. This method also separates them according to depth of production, and is closely related to Beatty's[1] method, of which it may indeed be considered a modern adaptation. As in his experiments, the cathode rays strike a thin sheet of a metal and the indirect rays come from a thick block of another metal, placed under the sheet. Thanks to the spectrometer, however, in order to distinguish the rays of one metal from those of the other, it is no longer necessary to use metals of very different atomic numbers. In fact, the more nearly alike they are, the better, so long as the lines of one can be resolved from those of the other. In the present experiments, therefore, the composite targets were made of sheets of silver laid on a block of cadmium.

Three such targets were used. One had two sheets of silver foil, made by Baker & Co., each 6 microns thick as judged by its absorption of X-rays, using Richtmyer's[5] absorption coefficients. Another had a single sheet of 6-micron foil, and the third a half-millimeter plate of graphite electroplated with silver to a thickness of 3.5 microns, also measured by absorption. These targets were placed so as to receive cathode rays at about 45° and send X-rays to the spectrometer with an emergence angle of 77°. Under these conditions they gave the spectra shown in figure 2, all taken with 0.07 ma. at 50 kv. and exposures of the chamber to the X-rays equal to 20 seconds.

To a first approximation, with extremely thin sheets of silver, all rays appearing in the silver lines might be regarded as direct; and if the cathode rays are all stopped before reaching the cadmium, all the cadmium rays must be indirect. With thicknesses such as these, suitable for stopping the cathode rays and for getting reasonably accurate intensity measurements without using cathode rays enough to damage the foils, a large correction must be made for the production of indirect rays in the silver and the consequent loss of opportunity for such action by the cadmium; and another correction must be made for the loss of cadmium rays by absorption in coming out through the silver. A third correction is for the

difference in the frequencies of their absorption limits, preventing the cadmium from making use of some of the rays that would be available for fluorescence in silver. A fourth, occurring in the third film only, is for the absorption by the graphite.

All these corrections are straightforward enough, theoretically at least, though the need for arithmetic integration makes it difficult to express them in formulas. The corrections for absorption of the cadmium rays in coming through silver, and for the loss of primary rays in the silver, are

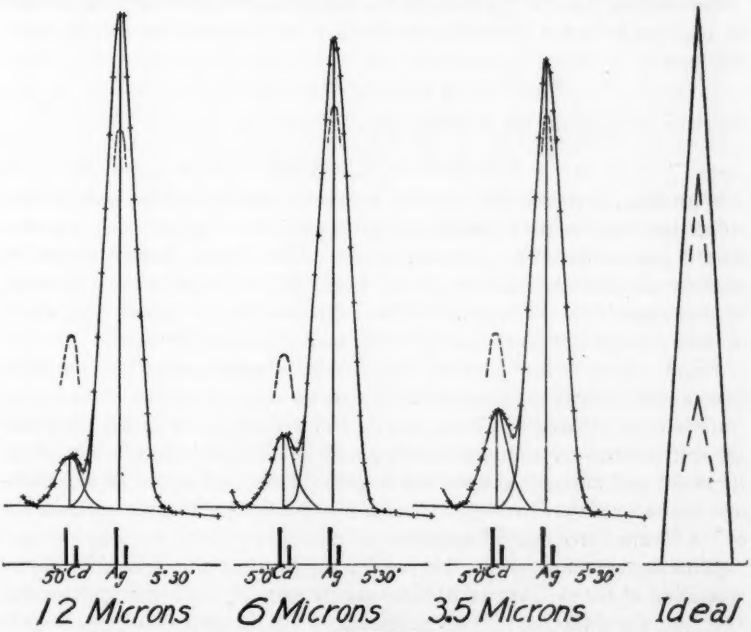

FIGURE 2

Kα peaks in spectra of composite targets of Ag on Cd, with thicknesses of Ag as indicated. Full lines, observed data; dotted lines, direct-ray and indirect-ray peaks deduced from these data.

made in one step, by partitioning the secondary rays between the cadmium and silver as if both the film and the block were made of silver. This is mathematically easy, because the ratio of the absorption coefficients of any two frequencies, primary and fluorescent, is practically the same for each of these metals, and it is done by simply splitting the triple integral given in section II for E''_α into two parts. Thus for a silver film of thickness x_1, the range of r for the silver is from zero to $x_1 \sec \psi$ for any given value of the colatitude ψ, and the cadmium has r from $x_1 \sec \psi$ to infinity.

The third correction, for the difference in absorption limits, is made by changing the lower limit of the frequency integral for cadmium, leaving that for silver fixed.

The fourth correction, for the effect of the graphite, is made by the use of absorption data taken by Mr. R. M. Yeatman for a thick block of graphite from the same piece from which this plate was cut. This plate stops about 2 per cent of the outgoing cadmium rays and about 1 per cent of the harder primary rays.

Calculating thus the fractions of the theoretical indirect rays that should be received from the cadmium, we find for the three cases, in order as in the figure,

$$E''_{\alpha Cd} = E''_{\alpha} \times 0.29-,\ 0.47-\text{ and } 0.56.$$

Likewise calculating the fractions produced in the silver,

$$E''_{\alpha Ag} = E''_{\alpha} \times 0.67,\ 0.44 \text{ and } 0.325.$$

With these fractions the observed cadmium peaks can be used to calculate the total indirect radiation from a solid silver target, shown as the dotted peaks above the cadmium peaks. Then these quantities can be used to calculate the indirect rays from the present silver foils, which can be deducted from the observed silver rays, leaving the direct rays alone, as shown in the dotted peaks under the observed peaks for silver.

Finally, the results of these calculations have been averaged for the three cases and are shown in an idealized form at the right-hand side of the figure. This represents what could be expected of a solid silver target, omitting the continuous spectrum and showing only the Kα peak, in full lines, with its direct and indirect components in dotted lines within it. In this average, the ratio of the direct rays to the indirect is 2.36, with a mean deviation of 7% for the three individual cases.

With regard to errors in this result, the greatest was probably in the spreading of the primary continuous-spectrum rays on their way from the silver to the cadmium. This occurred in the 12 and 6 micron targets because the silver foils would not lie flat when heated by the cathode rays, but became curved, raising the whole middle part of the foil about a millimeter; and in the third target, the graphite had a finite thickness.

To minimize this error, the source used was limited by the spectrometer slits to a width not over 1.5 millimeters, and the focus of the cathode rays, as measured across the plane of the slits, was made about a centimeter in diameter. Thus, whatever rays were lost to view from the spectrometer crystal by spreading out of the region used, the loss was probably almost balanced by the gain from rays coming into it.

Other errors, probably small, are due largely to differences in properties between cadmium and silver, other than those corrected for. Among such errors may be listed fluorescence produced by cadmium β-line rays

in the silver, contributing to the silver α peak an amount equal to a small fraction of the amount deducted as described above. Another error is due to the very small difference in the ratios between the absorption coefficients of rays of any two wave-lengths. Another is due to differences in the over-all sensitivity of the spectrometer and its accessories for rays of the α-line frequencies of the two elements. Finally there is an error, not of this type, due to lack of uniformity in the thickness of the silver films. How much this last error amounts to, it is hard to say. For the film on graphite, which was slightly rough, it may be considerable and it is difficult to estimate; for the foils, the presence of minute holes throws doubt on the assumption of uniformity, but absorption tests of two pieces showed average thicknesses equal within limits of error, about 2 or 3%.

With regard to other voltages than this 50 kv., Beatty's[1] work of 1912 showed for copper that the direct and indirect rays increased in much the same proportion, though in that case the ratio was about 6 or 7, some two or three times the value for this case. In rhodium, likewise, it has been noted before[7] that the total intensity of any line increased much as one might expect of indirect rays, though for a different reason. Preliminary work at 40 and 55 kv. with the 6 micron foil used here, showed practically the same ratio as in this work at 50, but as the current was less, due to a desire to find out the main facts before running too much risk of damaging the target, the results are not so exact.

The study of this direct-to-indirect ratio is being continued, using other voltages, and will be reported more fully. In the meantime, it is safe to assume that a value of 2.4 at 50 kv., about twice the excitation voltage, is fairly representative of the ratio for silver at all ordinary X-ray voltages.

IV. *Ratio of Indirect Rays to the Continuous Spectrum.*—The assumption that the ratio of direct to indirect rays is approximately constant at 2.4, for all voltages, leads at once to the inference that in the emergence-angle experiments of section II, the values observed for A/C should bear a ratio to the calculated values of A''/C something like 3.4. Actually, at the 20° emergence angle, where A'' is least affected by absorption, the ratio is somewhat less than 3.4, but of the right order of magnitude.

A more reliable check on calculated values for A''/C can be obtained from the 50 kv. data of section III, where the values of A'' are given by the corrected cadmium peaks, without reference to A'. The theoretical value of E''_α is $\frac{1}{2} K u_\alpha \nu_\alpha \nu_K \times 0.338$, where the symbols are as defined in section II and the 0.338 is the result of arithmetic integration for the special case of 50 kv. Therefore,

$$\frac{A''}{C} = \frac{\frac{1}{2} u_\alpha \nu_K \times 0.338 \tan \theta}{\nu_0 - \nu_\alpha + B\nu_\alpha}.$$

This gives numerically, 28.4′, and the experimental value, for the average of the three cases, is 30.2′.

The ordinate C was itself only 30.5 mm. and the electrometer was liable to erratic variations of a millimeter or two either way, resulting apparently from the fluctuations in numbers of α and β rays producing the natural ionization. Thus errors in C alone might readily account for the difference between these figures, and there are several other sources of error in the calculation, especially assumptions (1) and (10) of section II, capable of producing more error than this. The agreement found here must, therefore, be discounted somewhat, but it shows that the basic ideas are not unreasonable. When the form of the continuous spectrum and its distribution in space are more exactly known, such calculations may prove useful as a check on determinations of the fluorescent efficiency constant, u_α; or conversely, since Balderston's u_α is probably the better known factor at present, they tend to confirm the above assumptions about the continuous spectrum.

V. *Fluorescent Rays in Thin-Target Spectra.*—An important problem, on which these data throw some light, is that of line spectra from thin targets, and the relations of their intensity to voltage. Bergen Davis[8] proposed a method of getting such data by using thin films of silver plated on copper; and in a research in progress in this laboratory the method has been found quite practical. If, however, it had appeared here that nearly all the line-spectrum rays from a thick target were indirect, such rays as came from the thin target might well contain an unknown amount of indirect rays, due to continuous-spectrum rays from the copper. According to the present calculations, if the silver is made well under a micron thick, as it must be for cathode-ray penetration without undue loss of speed, the line-spectrum rays from it are nearly all direct; the next step, to eliminate the indirect rays almost completely, is to reduce the continuous-spectrum rays by replacing the copper with beryllium.

VI. *Quantum Probability Ratios.*—When a cathode ray passes through an atom, it may lose a large fraction of its energy, either in ejecting an atomic electron or in emitting a quantum of continuous-spectrum radiation, but there is no other obvious way for it to lose energy in anything like such large quantities. Consequently one may well inquire whether either one of these types of action occurs very much more often than the other and, if so, which?

To make the question more definite, since the ejection of an electron cannot occur without the loss of at least as much energy as $h\nu_K$, we may best compare the probability of the ejection of a K electron with that of emitting any continuous-spectrum quantum of frequency above ν_K. In view of the confirmation of the theoretical relations between A'' and C, noted above, it seems reasonable to apply to this problem the same basic assumptions used for that.

The number of continuous-spectrum quanta of the required range of frequencies is of course readily found as

$$N_C = 4\pi \int_{\nu_K}^{\nu_0} \frac{I(V, \nu)}{h\nu}\, d\nu = \frac{4\pi K}{h} \left\{ (\nu_0 + B\nu_\alpha) \log \frac{\nu_0}{\nu_K} - \nu_0 + \nu_K \right\}.$$

The number of direct α-line quanta is

$$N'_\alpha = \frac{4\pi E'_{\alpha 0}}{h\nu_\alpha}$$

where $E'_{\alpha 0}$ is the intensity of direct characteristic rays as emitted from the atoms. The correction for absorption, to get $E'_{\alpha 0}$ from E'_α, may be estimated from earlier data on molybdenum to be not over 1.02, and is unimportant. It will, therefore, be neglected here. This quantity N'_α is, of course, less than the number of K electrons directly ejected, which we may call N'_K, partly because some of the K-series energy is in the β and γ lines and partly because some K ionizations result in secondary photoelectrons rather than quanta of characteristic rays. Since the subsequent disposal of any ionization energy by an atom is probably independent of the method of ionization, we may assume that the ratio N'_α/N'_K is the same as N''_α/N''_K, which by definition is u_α.

Now let P equal the ratio of the direct radiation to indirect, determined above as 2.4, and Q the ratio to be finally determined, namely that of the number of direct K ionizations to the number of continuous-spectrum quanta of frequency above ν_K. Then

$$Q = \frac{N'_K}{N_C} = \frac{N'_\alpha}{u_\alpha N_C} = \frac{4\pi E'_\alpha}{h\nu_\alpha u_\alpha N_C} = \frac{4\pi P E''_\alpha}{h\nu_\alpha u_\alpha N_C}.$$

Inserting the value of E''_α as calculated from the integral of section III, and that of N_C just given, this becomes, for 50 kv.,

$$Q = \frac{\frac{1}{2} \times 0.338\, P}{\frac{\nu_0 + B\nu_\alpha}{\nu_K} \log \frac{\nu_0}{\nu_K} - \frac{\nu_0}{\nu_K} + 1},$$

where the 0.338 is, as in section IV, a result of arithmetic integration for this special case. For this case, with $P = 2.4$ and $\nu_0 = \frac{e}{h} \times 50$ kv., this has the numerical value

$$Q = 0.965.$$

The fact that this particular value of Q is equal within limits of error to unity suggests that Q may possibly be unity always. This idea, however, is probably false. For if it were true, and a comparison were made of different elements at corresponding voltages, that is, equal values of

ν_0/ν_K, the value calculated for Q would be practically proportional to P and, as we have seen, Beatty's data for copper make P two or three times as large as in the present work on silver. A check on this comparison may be obtained from Unnewehr's[2] data on ratios of the type A/C for various elements including these two, from which one may calculate the ratios of A to the continuous-spectrum energies in corresponding intervals of the spectrum. These ratios must differ qualitatively much like the values of $(1 + P)$, and the data at hand confirm, so far as they go, the above conclusions about the changes in P and Q from one element to another. On this topic, however, more work is needed before definite laws can be formulated. The important points for the present are: first, that Q, the ratio of the numbers of losses of energy from cathode rays, by direct K ionization and by corresponding continuous-spectrum radiation, is probably not constant for different metals; and second, in the absence of information on the point, no definite statement can be made as to the variation of Q with voltage for any one metal. For the case tested, silver at 50 kv., its value is nearly unity.

VII. *Summary.*—1. By experiments of two types (sections II and III) it has been proved that the characteristic rays from silver are largely of direct origin, the experiments of the second type giving a ratio of direct rays to indirect equal to 2.4 at 50 kv., nearly twice the excitation voltage.

2. The ratio of indirect radiation to continuous-spectrum radiation can be calculated reasonably accurately (section III) from known data on the form of the continuous spectrum and the fluorescent-energy transformation constant.

3. Indirect rays will not appear notably in spectra from extremely thin targets, especially with light backing materials for the targets (section IV).

4. The ratio of the probability that a cathode ray will remove a K electron from some atom by direct action to the probability that it will radiate a quantum of energy in the continuous spectrum as great as the K ionization energy, is of the order of unity for silver at 50 kv. It is probably greater for copper under corresponding conditions and may vary somewhat with voltage (section VI).

In conclusion, I wish to express most hearty thanks to Professor L. S. Jacobsen and Messrs. B. G. Stuart and R. H. Varian for assistance in making these measurements.

[1] R. T. Beatty, *Proc. Roy. Soc.*, **A87**, 511 (1912).
[2] Mark Balderston, *Physic. Rev.*, **27**, 696 (1926).
[3] W. R. Ham, *Ibid.*, **30**, 1 (1910).
[4] D. L. Webster and Hennings, A. E., *Ibid.*, **21**, 301 (1923).
[5] F. K. Richtmyer, *Ibid.*, **27**, 1 (1926).
[6] D. L. Webster and Hennings, A. E., *Ibid.*, **21**, 312 (1923).
[7] D. L. Webster, *Ibid.*, **7**, 599 (1916).
[8] B. Davis, *Ibid.*, **11**, 433 (1918).

MUCRONATE ELECTRODE WITH MICROMETER*

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1. *Apparatus and Data.*—The adjustment is shown in figure 1 where the electrode E' is attached to the $^1/_4$ inch brass tube a, partially stopped at c by a perforated cylinder. The tube a contains the micrometer screw b, the end of which is tipped by the needle n. Hence by turning b, the point n may be moved from within $E'c$, and made to project by any small amount beyond it. The zero of this apparatus is arbitrarily found at the position of the micrometer screw (reading y), at which pressure s suddenly begins to appear at E, measured by the U-gauge beyond U. Before this sparklets (sputtering) continually jump across from E' to E and $s = 0$. The first stable s (for $y = 0$) is often casual, the fringe displacement s appearing and vanishing alternately with much interferometer turmoil. Immediately thereafter (Figs. 2, 3, 4), y increasing, s is definite and near the maximum. Over half the efficiency is usually lost after the point projection $y = 1$ mm.

The relatively low s values in the earlier work indicated some maladjustment. The electrodes E and E' were, therefore, freshly turned, polished and adjusted more fully in parallel. The effect of this is astonishing as shown in the graphs, figures 2, 3. Both graphs drop from an actual cusp for the initial data were

$y = 0.02$	0.025	0.03	0.04 cm.	}	etc.
$s = 0$	560	520	480	}	

At $y = 0.025$ the sparking is so imminent that it is difficult to catch the fringes between sparks. At $y = 0.02$, $s = 0$ and, therefore, the point of the needle is just within the effective surface of the disc electrode; so that the cusp appears within a tenth of a millimeter from the effective limit. Had it been possible to approach this closer, there is no doubt that a higher order of s-values would have been obtained. The field for $x = 2$ cm. may be estimated as 10 *kv./cm.* ensuring the stream of ions just before sparking.

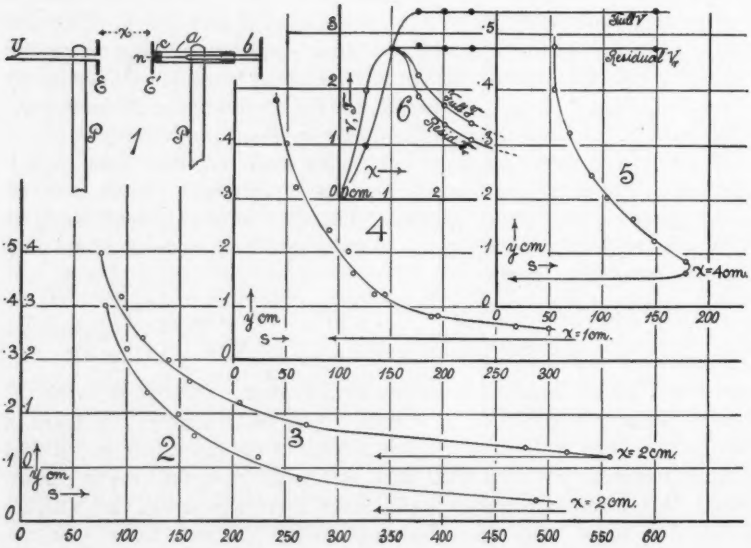
The corresponding phenomena for other spark gap (x) values are now to be treated. In figure 4, $x = 1$ cm. while y increases from 0 to nearly 0.5 cm. At this small distance sparks readily jump across and they pass between parts of the electrodes rather than from the salient needle point. At times sparking may suddenly cease whereupon high pressure (s) at once takes its place. Thus there is no doubt that this graph is cuspidal,

* Advance note from a Report to the Carnegie Institute of Washington. Cf. *Science*, 1927, pp. 448–50, vol. lxv.

though it could not be tested. The s-drop with increasing y is naturally fast, and $s = 0$ would soon occur since $x-y$ is small.

The case for $x = 4$ cm., figure 5, differs from curve a, as in the former the cusp seems to be actually rounded. The s of the crest, moreover, is less than was expected (cf. Figs. 2, 3).

When the needle retreats into the effective confines of the E' electrode, the latter begins to sputter. At smaller distances sparks may pass across. The pressure s drops to zero very nearly. This sputtering following high s values when y is small is very interesting, since it recalls the behavior of the sensitive flame in acoustics. Here also a uniform linear column breaks down into an oscillating or turbulent condition. If in sputtering the ionized winds are alternately positive and negative they would produce no pressure at E.



Alternatively one may simply assert that the field insulation breaks down when the electrical pressure or field potential energy, $F^2/8\pi$, has reached a certain value. The energy which drives the air current is then converted into the heat of the minute sparks and the electric wind ceases. In the absence of sputtering, the ions are taken from E' to E by air convection; hence the pressure s. On the other hand when sputtering occurs and $s = 0$, the electric current phenomenon is akin to the conduction of electricity in electrolytes though with far more tempestuous collision of ions.

A series of experiments in which the actual saliency y' of the needle from the plane of the electrode E' was measured (in the preceding graphs, Figs. 2, 3 4, the $y = 0$ refers to the first occurrence of sputtering) gave the following data:

$x = 2$ cm.; y'	$= 0.03$	0.05	0.06	0.07	0.11	0.19	0.27	cm.
s	$= 0$	0	570	480	320	190	140	

Thus sputtering begins when the needle protrudes half a millimeter from this electrode. Endeavors made to sharpen the rather fine needle brought no consistent results.

A needle placed in the U-tube electrode E and removed from the other, E', produced only a just perceptible negative pressure.

2. *Miscellaneous Results.*—Some relevant measurement of the potential variation of the machine is desirable to accompany the preceding results. These data were obtained with a simple electrometer in which the indications were given by the deflections of a light horizontal flexure needle of aluminum. It was not thought necessary to standardize the apparatus as the deflections suffice the present purposes. One pole of the Winshurst machine was put to earth and the other joined to the electrometer. An example of the results is given in figure 6, in which the potential is rated in arbitrary scale parts for different widths x of mucronate spark gap. The graph V shows the free potential with the machine making 6 rotations per sec. V_r is the residual potential retained after the machine comes to rest ($r/t = 0$) without being discharged. This is the threshold potential and the electric wind of the preceding paragraphs does not blow ($s = 0$), until this potential is exceeded. One may note in particular that V is constant after $x = 1.5$ cm. for the mucronate electrode used. For $x < 1.5$ cm. the V and V_r values are coincident and fall off very rapidly.

If we write $F = V/x$, treating the axial field, F, as uniform, the graphs F and F_r are obtained. Both curves have their crests at $x = 1$ cm., which should, therefore, be the strongest field used. In the preceding experiments (*Science*, loc. cit., s, x graphs), the electric wind crests occurred at $x = 2$ to 2.5 cm., therefore, in a materially weaker field F. It is to be observed, however, that for $x = 1$, the electrodes are already so close together that the electric wind must in large measure be radially outward. Hence only a component pressure acts at the electrode E. Not until the value of x has become larger ($x = 2$) will the wind in the main be axial.

It is somewhat surprising that the limiting potential is practically independent of the speed of the machine. Thus far spark gaps $x = 1.5$, 2.0, 4.0 cm. each at rotations 1.5, 3, 6 rot./sec. the same limiting potential was built up, more gradually, of course, for the slower motions.

The endeavor to use the mucronate electrode in case of an induction coil just below sparking, in a given gap, did not succeed. Values of s

between $s = 7$ and 15 finally $s = 30$, could be obtained for $x = 3.5$ cm.; and there was even then much sputtering.

It remained to determine the effect of the speed of rotation (r/sec.) of the given electric machine on the s-values.

When x is constant, s increases nearly proportionally to the angular velocity of the plates, 1.5, 3 and 6 rotations of each plate per second being instanced. The lines pass through zero as x increases from 0 to 1 to 2 cm., the optimum spark gap. The rates at which s increases with r/sec. thus steadily increase. After this ($x = 2$ to 4 cm.) the line merely drops, the rate of s increase with r/sec. remaining about the same. Thus, for instance, if $x = 4$ cm. 1.5 rotations per second leave s unchanged at zero.

The effect of this on the sx graphs is apparent: the crests persist at $x = 2$ cm.; but that the graphs drop as a whole when r/s diminishes from 6, to 3, to 1.5 rot./sec.

3. *Velocity of the Winds.*—An estimate may perhaps be obtained if we use Bernoulli's equation and put $v = \sqrt{2p/\rho}$. In the graphs, figures 2, 3, 4, the s-values at cusps are very commonly $s = 300$ and they mount to even $s = 550$. Since the unit of s is about 10^{-6} atm., these data may at once be taken as pressures in dynes/cm.[2] Thus the velocities in the two cases are $v = 770$ cm./sec. frequently and $v = 1000$ cm./sec. in very favorable cases. These are astonishingly large values. In the small time of x/v where $x = 6$ cm., there is very little time for the decay of ions. The change of s with x is thus to be associated with a ring-shaped vortex of air, whose axis or line of symmetry is the needle prolonged. Hence the currents near the electrode E, when x is small, must be largely radial and outward as already instanced. The bearing of much of this, on the cathode minimum potential, will be treated later.

THE REFLECTION OF ELECTRONS FROM CRYSTALS

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The recent experiments of Davisson and Germer[1] on the reflection of electrons from a crystal of nickel have shown a strong analogy between this phenomenon and the reflection of X-rays from the same crystal; the analogy is not complete, however, and the essential differences may be summarized in the following two hypotheses.

I. A single plane of atoms reflects a very appreciable fraction of the electron wave, whereas the same plane would reflect only an inappreciable part of an X-ray wave.[2]

II. The wave-length of the electron wave in the interior of the crystal is not the same as the wave-length of the same wave in free space, as is the case (practically speaking) for X-rays. This corresponds to the assumption of an index of refraction for the electron wave.

The fundamental hypothesis of the wave-mechanics is that the wave-length of the electron wave in free space is $\lambda = h/mv$. Let us first consider the limiting case in which the first plane of atoms on the surface of the crystal reflects all of the wave and none of it penetrates the interior. Then the general theory of interference from a plane of atoms[3] predicts that if the incident beam is normal to the surface of the crystal beams will be reflected in all azimuths perpendicular to lines of atoms in the plane. This is in agreement with figure 2. (Davisson and Germer, loc. cit.) The co-latitude θ of the beam is determined by the formula

$$d \sin \theta = n\lambda$$

where d is the distance between the corresponding lines of atoms on the surface of the crystal (*not the distance between planes in the interior*). The data of the last three columns of table 1 (loc. cit.) were calculated from this formula. It is also in quantitative agreement with figure 1 (loc. cit.)—a fact which appears to have been overlooked.

In the actual case, where the first plane reflects only a fraction, say α, of the incident intensity, the second will reflect $\alpha(1 - \alpha)$, the third $\alpha(1 - \alpha)^2$, etc.; this will not affect the previous results, but we are, in addition, enabled to calculate the intensity in the various beams. The amplitude of the reflected wave will be proportional to the absolute value of

$$\alpha \sum_{n=0}^{\infty} (1 - \alpha)^n e^{2\pi i n\gamma/\lambda'} = \alpha/[1 - 2(1 - \alpha) \cos (2\pi\gamma/\lambda') + (1 - \alpha)^2]^{1/2}$$

where $n\gamma$ is the retardation in path of the wave reflected from the nth plane relative to the wave reflected from the first plane, and λ' (equal to λ/μ say) is the wave-length in the interior of the crystal. If c is the distance between successive planes of atoms parallel to the surface, $\gamma = c(1 + \cos \theta)$.

This expression for the amplitude of the reflected wave has a maximum when

$$\gamma = c(1 + \cos \theta) = m\lambda/\mu.$$

If we take $\mu = 1$, this is also the position of the corresponding X-ray beam, which is not in agreement with the observed facts; but if we take $\mu = 0.7$, then the formula correctly summarizes the data of table 1, columns 4, 5 and 6 (loc. cit.).

The theoretical interpretation of the constants α and μ must be the object of any more detailed treatment of the subject.

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[1] *Nature*, 119, 558 (1927).

[2] This hypothesis was suggested to the author in conversation with Dr. F. Zwicky.

[3] Sommerfeld, "Atombau," 4th ed., p. 222.

COUPLING OF ELECTRONIC AND NUCLEAR MOTIONS IN DIATOMIC MOLECULES

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While for many important problems the quantum mechanical coupling between the motion of the nuclei and of the electrons in a diatomic molecule may be ignored, there are others in which this coupling is the main factor. Among the various phenomena which are conditioned by this coupling and which have recently attracted attention the following may be mentioned:

1. The mechanism of the dissociation of molecules by light absorption. This question has been discussed by Franck who, with his co-workers, is also doing important experimental work in this field.[1]

2. The mechanism of dissociation of molecules as a primary consequence of excitation by electron collision. The ideas of Franck on (1) have here been applied by Birge and Sponer[2] to a discussion of the experimental results of Hogness and Lunn.

3. The relative transition probabilities for the various vibrational transitions associated with a single electron transition in the emission or absorption of light by a molecule; i.e., the problem of intensity distribution in electronic band systems. This question has been treated recently by the writer.[3]

4. The mechanism of the process whereby molecules may be excited to vibration levels by electron collision without simultaneous electronic excitation. That this process actually occurs is proved by the recent experiments of Harries, carried out in Franck's laboratory.[4]

All of these phenomena permit of being understood in terms of the new quantum mechanics, at least in a qualitative way, as it is the purpose of this note to show.

The complete quantum-mechanical problem of a diatomic molecule, from the Schrödinger point of view, calls for the solution of a partial differential equation in $3N + 6$ independent variables, if N is the number of electrons in the molecule. The problem is distinguished from the prob-

lem of a complicated atom, by the presence of two particles of large mass, instead of one. The usual theory of the diatomic molecule, however, replaces the actual model of two nuclei and N electrons affecting each other with Coulomb forces by one which consists simply of two masses affecting each other by a more or less arbitrary potential energy law. This effective potential energy is supposed to result from the average of the reactions of the rapidly moving electrons on the nuclei together with the mutual Coulomb repulsion of the nuclei.

The known success of this simpler model in explaining the energy levels, in general, and the infra-red transition probabilities, makes it natural to suppose that the heavy masses of the nuclei bring about a partial or approximate separation of variables in the Schrödinger equation. The three coördinates which correspond to the motion of the center of gravity of the system in space are readily separated out. Similarly, if rotation is neglected, the system is described by the nuclear separation, R, and the electronic coördinates, denoted in the aggregate by X. The assumption of partial separation of variables here made requires the two following results:

(*a*) The energy-levels (eigen-wert parameter) are the sum of a function depending only on the electronic quantum numbers, denoted in the aggregate by e, and a function of both the electronic quantum numbers and a vibrational quantum number, n.

(*b*) The amplitude function, ψ, is the product of two factors, one of which depends on all of the quantum numbers and only the nuclear separation, R, while the other depends only on the electronic quantum numbers and the electronic and nuclear coördinates. That is, one has

$$E = E_1(e) + E_2(e, n)$$

$$\psi(e, n, X, R) = \psi_1(e, X, R)\cdot\psi_2(e, n, R).$$

This assumption, of course, needs justification in terms of the theory of the Schrödinger equation. An attempt to do this is being made. But, making the assumption, the four coupling phenomena already listed come within a single picture.

Numbers 1 and 3 are simpler than 2 and 4 for radiative transitions are simpler than those involving electron collisions. For the purpose of computing such transition probabilities one has to consider the matrix component of the electric moment of the molecule with regard to the initial and final state. This matrix component, referring to the initial state e', n' and the final state e'',n'', is given by

$$M(e'e''n'n'') = \int\int M(X, R)\psi(e'n'XR)\psi(e''n''XR)dXdR$$

in which $M(X, R)$ is equal to the electric moment of the molecule in the configuration X, R. The integration is over all values of the coördinates.

For the purpose of comparing various vibration transitions associated with the same electronic transition, one may perform the integration over the electronic coördinates. One obtains thereby an effective electric moment function, $m(R)$, for computing the different vibration transitions. The complete matrix component is then the integral of this moment function over the product of the two vibrational factors of the amplitude function.

The vibrational factor in this formula may safely be identified with the amplitude function obtained from the simple anharmonic oscillator treatment of the molecule problem. These amplitude functions have the essential characteristic that they approach a zero value asymptotically, but rapidly, outside of the region of the corresponding classical motion. Inside this region they oscillate, having as many zeros as the order of the quantum state. *Herein lies the quantum mechanical justification of the picture used by Franck* in discussing the dissociation of molecules by light absorption, and which has found application in the theory of transition probabilities in electronic band systems.

The Franck picture is that the favored transitions are those for which the classical vibrational motions cover over-lapping regions of the nuclear separation coördinate. Clearly this comes out of the quantum mechanical treatment by the property of the Schrödinger amplitude function of having its largest values at the coördinate values covered by the classical motion. Hence the larger values of the matrix components are, in general, those for which both amplitude function factors in the integrand have large values for the same values of the independent variable; i.e., those of over-lapping classical motion. The quantum-mechanical formula differs in two respects from the earlier treatment. One is that transitions of small probability corresponding to non-over-lapping classical vibration motions are made possible by the fact that the Schrödinger amplitude functions have values outside the range of the classical motion. Also, since the amplitude function oscillates within the range of the classical motion there is the possibility of a kind of interference in the transition probabilities, reducing the value associated with a transition which corresponds to over-lapping classical motions. This may be the explanation of the irregular alternations of intensity in the Wood's resonance spectrum of iodine, already discussed by Lenz in terms of the old correspondence principle for intensities.

To illustrate the semi-quantitative numerical behavior of the new quantum mechanical formula, two cases have been worked out roughly. For the purpose, $m(R)$ was regarded simply as a constant and the vibrational amplitude functions were taken to be the Hermitian polynomial harmonic oscillator solutions.[5] The harmonic oscillator solutions depend on the initial and final electronic state through the vibration frequencies

and centers of oscillation associated with the two states. The relative transition probabilities are measured by the product of the square of the matrix component and the fourth power of the quantum frequency involved, in accordance with the classical dipole radiation formula.

Thus, applied to the $n' = 0$ progression of the Schumann-Runge bands of oxygen, one obtains for the relative intensity of the bands corresponding to various final state vibration quantum numbers, n'':

n'' =	0	1	2	3	4	5	6
	8.4×10^{-6}	9×10^{-5}	5×10^{-4}	1.6×10^{-3}	6.6×10^{-3}	0.008	0.019

7	...	13	15	17
0.03	...	0.88	1.00	1.13

Experimentally, Runge measured on his plates only the bands $n'' = 11$ to $n'' = 17$, as being the strongest. This is in good semi-quantitative agreement with the foregoing calculations.

On the other hand, *SiN* offers a band system characterized by a very slight change in moment of inertia and frequency of vibration between the two electronic states.[6] Correspondingly, zero change in the vibration quantum number is the most probable. This comes out of the matrix formula since, had there been no change in moment of inertia or natural frequency, the two amplitude functions in the formula would have been members of the same normal-orthogonal set of functions, so that only the zero vibration change would be allowed. When this is "almost" the case, the functions are "almost orthogonal" thus favoring the zero change in vibrational quantum number.

Turning now to the coupling processes 2 and 4, one may interpret these in essentially the same way as a consequence of Born's quantum mechanical analysis of the problem of the collision of a charged particle with an atomic or molecular system.[7] A free electron colliding with a molecule interacts with each of the electrons and the nuclei in the molecule according to the Coulomb law. If this energy of interaction be developed in negative powers of the distance of the electron from the center of gravity of the molecule, the development begins with an inverse cube term representing the interaction between the free electron and the dipole moment of the atom. The higher powers of the development correspond to the interaction with the quadrupole and higher moments of the electric charge of the molecule. When these are neglected, Born's analysis shows the probabilities of excitation of a molecule by electron impact are proportional to the square of the matrix component of the electric moment of the molecule in regard to the initial and final states in question. This, however, is the same quantity as that which measures the probabilities of transition associated with light emission and absorption. Therefore, to the order of approximation which replaces the

electron interaction with the molecule by that between the electron and equivalent dipole, one has that vibration transitions associated with electronic excitation of the molecule will be the same whether the process is radiative or a result of a collision. This is the justification of the argument of Birge and Sponer in discussing the experiments of Hogness and Lunn.

Using this same analysis of the collision problem, it is clear that the action of a colliding electron on a molecule in exciting vibration transitions without electron excitation, the fourth type of coupling in the list, is a consequence of the non-vanishing of the same matrix components as those which measure the probability of vibration transitions in infra-red, vibration-rotation bands. The correlation is, however, not a sharp one, for in the collision process the electric moments of higher order of the molecule may be active.

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[1] Franck, *Trans. Faraday Soc.*, **1925**; Dymond, E. G., *Zeits. Phys.*, **34**, 553 (1925); Kuhn, H., *Zeits. Phys.*, **39**, 77 (1926).

[2] Birge and Sponer, *Phys. Rev.*, **28**, 259 (1926).

[3] Condon, E., *Ibid.*, **28**, 1182 (1926).

[4] Harries, W., Preliminary report at meeting of the Deutschen Physikalischen Gesellschaft, Hamburg, Feb. 6, 1927.

[5] Schrödinger, *Ann. Phys.*, **79**, 514 (1926).

[6] Compare treatment and discussion in *Phys. Rev.*, **28**, 1182 (1926).

[7] Born, *Zeits. Phys.*, **38**, 803 (1926).

WAVE MECHANICS AND THE NORMAL STATE OF THE HYDROGEN MOLECULE

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The problem of the motion of a particle attracted by two fixed centers of force according to the Coulomb force law can be treated by classical mechanics and has been used in quantum theory by Pauli and Niessen for a theory of the hydrogen molecule ion.[1] In the quantum mechanics, where the energy levels are determined as the "eigenwerte" of Schrödinger's equation, the variables are separable and the boundary value problem is easily set up. But thus far a satisfactory treatment of the differential equations involved is lacking. Burrau[2] has recently carried out a numerical integration of the problem for the lowest energy level of an electron moving under the influence of two fixed centers of Coulomb attraction as a function of the distance apart of these centers. In this paper, Burrau's

data are used to give a semi-quantitative discussion of the neutral hydrogen molecule. His values are:

Nuclear separation	1.0	1.3	1.6	1.8	2.0	2.2	2.4	2.95
Electronic energy	2.896	2.648	2.436	2.309	2.204	2.109	2.025	1.836

The unit of separation is the Bohr 1_1 orbit radius of hydrogen atom, that of energy is the ionization potential of atomic hydrogen.

In all this work the tacit assumption is made that, because of the large masses of the nuclei, the problem can be solved regarding the nuclei as fixed at a distance which is one of the parameters of the problem. When the energy of the electronic motion as a function of the distance is known, the energy of the Coulomb repulsion of the fixed nuclei is added and so the variation of the total energy of the non-rotating non-vibrating molecule with nuclear distance is found. The minimum of this curve is taken as the "equilibrium" separation of the nuclei and the value of the minimum is taken as the energy of the molecule in that electronic state. (More correctly, the small amount $^1/_2h\nu$ is to be added to the minimum value.) If the nuclei are no longer regarded as fixed this curve is regarded as giving the "law of force" governing the rotational and vibrational motions of the molecule. That this is the correct procedure in the classical mechanics was shown by Born and Heisenberg:[3] that it remains correct in the quantum mechanics has not yet been definitely proved. There is no reason to believe, however, that it is not correct, and it will be used here without further justification.

When the nuclei of a hydrogen molecule ion are far apart one is dealing virtually with a free hydrogen atom and a proton. The electronic energy is then mainly that of the Coulomb interaction between the proton and the electronic charge of the atom. If the atom were not Stark-affected by the proton, this would be just equal to the nuclear repulsion and the total energy would be simply R for all values of the nuclear separation (all values are negative), where R is the Rydberg constant. But the proton induces a polarization of the H-atom and, therefore, the energy of proton-electron interaction is greater than that of proton-proton. On the other hand, when the nuclear separation is zero and the electron moves under the influence of a double central charge, the energy is that of the lowest state of ionized helium. Burrau's numerical integrations supply values of the electronic energy for intermediate electronic separations. When the nuclear repulsive energy (curve *b*, Fig. 1) is added to Burrau's values there results curve *a*, figure 2, which is Burrau's curve for H_2^+. The equilibrium separation is 2 units (i.e., 2 times the radius of the Bohr 1_1 hydrogen orbit) and the minimum energy is $1.204\ R = 16.28$ volts. The heat of dissociation is $0.204R = 2.76$ volts. Burrau checks the value with experiment by an indirect comparison with the ionization potential of H_2 as discussed later in this paper.

Turning now to the neutral molecule one expects, on the Pauli principle of assigning quantum numbers, that the two electrons will be in equivalent orbits. The starting point, therefore, for the approximate treatment of the problem is a model in which the two electrons have no mutual influence and each moves as it would if alone in the ground state of H_2^+ as given by Burrau. The electronic energy of this model at each distance is evidently just twice that for H_2^+. This curve of doubled H_2^+ values is given here as *a* of figure 1. Combined with the Coulomb proton-proton energy this yields curve *b*, figure 2, for the energy curve of the neutral H_2 molecule with uncoupled electrons. This gives an equilibrium separation of 1.075 units, i.e., a moment of inertia of 2.7×10^{-41} gr. cm.^{2} The heat of dissociation is $1.800R = 24.36$ volts.

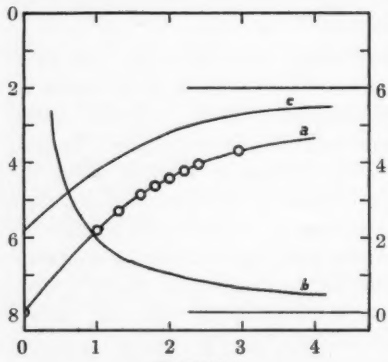

FIGURE 1

Electronic and nuclear energy in H_2. *a*, Values for non-interacting electrons. *b*, Coulomb energy of nuclear repulsion. *c*, Approximate electronic energy curve for interacting electrons. Units: ordinates, 1 = Rydberg constant, abscissas, 1 = radius of first Bohr orbit in hydrogen atom.

Naturally, such a model gives only a very rough approximation to the truth. But it is to be observed that the above model does set a definite lower limit on the moment of inertia of the molecule. For the electronic interaction, whatever its amount, will be positive and will decrease monotonously with increasing nuclear separation, since it is the repulsive potential of interacting-like charge. It acts to increase the ordinates of curve *b*, figure 1, by decreasing amounts and, therefore, shifts the minimum of the resultant curve to larger abscissas. This seems to be an important conclusion inasmuch as *the lower limit here definitely given by quantum mechanics is greater than nine of the thirteen values obtained on various theories from specific heat data* as presented in the recent thorough review of the the subject by Van Vleck and Hutchisson.[4]

Turning now to the electronic interaction, the analysis of Hund[5] provides the important result that the electronic term of the lowest state of a molecule changes continuously from its value for a neutral atom of equal number of electrons to its value for the dissociated atoms, according to the new quantum mechanics. Herein lies an important difference between the old and the new quantum theory which is essential to the argument of this paper. That unexcited molecules dissociate into two unexcited

atoms as a result of vibrations of infinite amplitude has been shown empirically by Birge and Sponer.[6]

The first approximation to the electron interaction in unexcited helium has been computed by Unsöld,[7] by means of the wave mechanics, who finds 5.5 R for the whole atom, i.e., 1.5 R = 20.3 volts for the ionization potential. Empirically the value is 5.818R for the total energy. At large distances the model goes over into two neutral hydrogen atoms. The electronic energy will, therefore, be asymptotically equal to the Coulomb interaction of an electron and a proton, for it is made up of the repulsion of the two electrons and the attraction of each proton for the electron of the other atom. Moreover, the situation is now that of the interaction of two neutral units so that polarization deformation of each atom by the other will be much smaller than in the case of H_2^+. Inasmuch as Burrau's work shows that at a distance of 2.95 units the electronic part of the H_2^+ energy differs from the pure Coulomb by about 0.1 R, it is safe to assume for the H_2 molecule a closer approach to Coulomb value for abscissas greater than 3 units. For intermediate points, a natural assumption is to reduce the doubled Burrau value in the ratio 5.818:8.00 in order to secure agreement with helium. If this is done it is found that the resulting curve joins on to the Coulomb curve smoothly. Curve c of figure 1 has been drawn from the theoretical values so reduced up to the value for 2.4 and joined on to a Coulomb curve for abscissa values of 3 and greater.

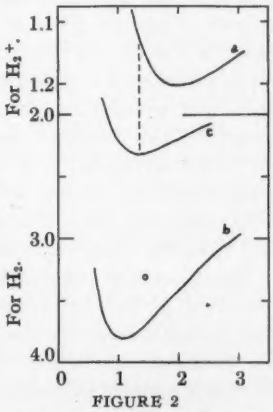

FIGURE 2

Resultant energy curves in H_2^+ and H_2. a, Burrau's curve for H_2^+. b, Curve for H_2 for non-interacting electrons. c, Approximate curve for H_2 with interacting electrons. The small circle in the crook of curve b, represents the equilibrium position and energy on Hutchisson's classical crossed-orbit model of H_2. Units: same as figure 1 (note different scales of ordinates for H_2 and H_2^+).

The result of combining c and b of figure 1 is to give c of figure 2 as the energy curve for the hydrogen molecule. The minimum of this curve corresponds to a moment of inertia of 4.26×10^{-41} gr. cm.^{2}, and to a heat of dissociation of 4.4 volts. The latter value agrees to within 0.1 volt with the band spectrum value of Witmer and of Dieke and Hopfield.[8] These figures should be compared with a moment of inertia of 4.91×10^{-41} gr. cm.^{2} and 1.422 R heat of dissociation found by Hutchisson[9] from a cross orbit model of H_2 on classical quantum theory.

Another interesting consequence follows from the relation of the H_2

energy curve to that of H_2^+. According to a principle put forward by Franck, changes involving the electrons in a molecule will affect the nuclei mainly indirectly through the change in molecular binding.[10] According to this view, the most probable event in an electron collision experiment by means of which an electron is removed from H_2, is the removal of an electron while the nuclei are at a distance of 1.350 units. This requires an amount of energy given by the difference between 2.325 R and the ordinate of the H_2^+ curve at 1.350, namely 1.125 R. This is the theoretical apparent ionization potential and amounts to 1.2 R or 16.2 volts in good agreement with the mean experimental value 16.1 given by Franck and Jordan.[11] On the other hand, the true energy of the process $H_2 \longrightarrow H_2^+ + e^-$, where H_2^+ is in the lowest state, is the difference between the ordinates of the minima of the H_2 and H_2^+ curves, i.e., 1.12 R = 15.2 volts, comparing favorably with value of Witmer and of Dieke and Hopfield from the ultra-violet band spectrum of H_2.

The theoretical value of the frequency of vibration, depending on the curvature of the curve at its minimum, is naturally more uncertain. Calculation shows that the curve gives a frequency of vibration of 5300 cm.$^{-1}$, about 20% higher than the value 4360 cm.$^{-1}$ from experiment.[8] As for the moment of inertia, while it is larger than most of the values from specific heat theories, it is in accord with the larger values which have been found by Richardson and Tanaka[12] from analysis of the hydrogen bands.

In conclusion it seems proper to emphasize that Burrau's calculation of H_2^+ and the extension here to H_2 constitute the first quantum-theoretic quantitative discussion of the binding of atoms into molecules by electrons—the valence forces of chemistry. The quantitative success of the new quantum mechanics in the face of the classical theory's failure must serve to lend strong support to the new methods.

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[1] For a review of the status of the H_2^+ and H_2 problems prior to the new quantum mechanics see Van Vleck, *Quantum Principles and Line Spectra*, p. 88. Also discussion by Kemble in last chapter of National Research Council Report on "Molecular Spectra in Gases."

[2] Burrau, *Danske Vidensk. Selskab. Math.-fys. Meddel.*, **7**, 14, Copenhagen (1927).

[3] Born and Heisenberg, *Ann. Physik*, **74**, 1 (1924).

[4] Van Vleck and Hutchisson, *Physic. Rev.*, **28**, 1022 (1926).

[5] Hund, *Zs. Physik*, **40**, 742 (1927).

[6] Birge and Sponer, *Physic. Rev.*, **28**, 259 (1926).

[7] Unsöld, *Ann. Physik*, **82**, 355 (1927).

[8] Witmer, *Physic. Rev.*, **28**, 1223 (1926); Dieke and Hopfield, *Zs. Physik*, **40**, 299 (1926).

[9] Hutchisson, *Physic. Rev.*, **29**, 270 (1927).

[10] Franck, *Trans. Far. Soc.*, **21**, part 3 (1925). See also discussion by Birge, p. 248 of National Research Council Report on "Molecular Spectra in Gases," and quantum mechanical treatment by Condon, these PROCEEDINGS, **13**, 462 (1927).

[11] Franck and Jordan, *Anregung der Quantensprünge durch Stosse.*

[12] Richardson and Tanaka, *Proc. Roy. Soc.*, **106A**, 663 (1924).

A NEW EQUATION FOR THE DISTRIBUTION OF RADIANT ENERGY

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From certain considerations based on Einstein's theory of light quanta, I have recently deduced[1] an equation for the entropy of radiation, as a function of energy density and frequency, which is identical with the one obtained by Planck. From this expression it would seem possible to proceed immediately to Planck's equation for the distribution of radiant energy, by using a method which has hitherto been regarded as unquestionably valid. The deduction, however, rests upon a certain tacit assumption, as may be seen by a brief review of the method used in Planck's "Theory of Heat Radiation."

Using the same notation as in the preceding article, U and S are the total energy and entropy of a hollow containing radiation, u and s are the corresponding densities, and u_ν and s_ν represent the rate of change of these densities with the frequency, as we proceed through the spectrum. Thus, in the total volume V

$$U = V \int_0^\infty u_\nu \mathrm{d}\nu \tag{1}$$

$$S = V \int_0^\infty s_\nu \mathrm{d}\nu \tag{2}$$

If the radiation is in thermal equilibrium the entropy is at a maximum. In other words, if we consider a slight variation in the distribution of energy, produced by increasing infinitesimally the energy in some parts of the spectrum and decreasing that in other parts, then the total change in entropy produced by this variation will be zero (to the same order of infinitesimals). That is,

$$\delta S = 0. \tag{3}$$

If the variation is subject to the conditions that volume and total energy are fixed,

$$\delta V = 0, \tag{4}$$

$$\delta U = 0. \tag{5}$$

From the preceding equations, bearing in mind that the operations indicated by "d" and "δ" are independent, we find that

$$\int_0^\infty \delta u_\nu \mathrm{d}\nu = 0, \tag{6}$$

$$\int_0^\infty \delta s_\nu d\nu = 0, \tag{7}$$

and the last equation may also be written in the form,

$$\int_0^\infty \frac{\partial s_\nu}{\partial u_\nu} \delta u_\nu d\nu = 0. \tag{8}$$

It is a well-known theorem of calculus that if

$$\int_{x_1}^{x_2} \varphi(x)\psi(x)dx = 0$$

for *all values* of $\psi(x)$ which are compatible with the condition that

$$\int_{x_1}^{x_2} \psi(x)dx = 0,$$

then $\varphi(x)$ must be a constant. Applying this theorem to equations (6) and (8) it follows that $\partial s_\nu/\partial u_\nu$ is a constant, and from this point Planck proceeds by methods of undoubted validity to derive his distribution formula.

The whole proof rests upon the unstated assumption that the only restriction upon δu_ν is given by equation (6). This is equivalent to assuming that every state of thermal equilibrium is completely determined by a single variable, such as density of radiant energy or temperature. This assumption that underlies the whole classical thermodynamics of radiation as developed by Wien and Planck is based upon no experimental or theoretical evidence.

It is obvious that if the law of conservation of photons[2] be accepted, the state of a system in equilibrium will be determined only when the density of energy and the concentration of photons are both given; but this law may at present, seem too radical for general acceptance. I shall, therefore, attempt to show that, without any further assumptions than those which have already been fully accepted, we may deduce the existence of states of true thermal equilibrium which are not comprised in the "thermodynamics" of Wien and Planck (cf. the equilibrium states discussed by Einstein[3] to which he applies the terms "aussergewöhnlich" and "improprement dit").

As in my preceding paper, we may define a function n_ν by the equation

$$n_\nu = u_\nu/h\nu, \tag{9}$$

and thence define two other quantities by the equations

$$n = \int_0^\infty n_\nu d\nu; \qquad N = Vn. \tag{10}$$

We may also for convenience and without any implications call N the number of photons. We then find, by introducing these quantities into the classical equations for the thermodynamics of radiation, that whenever radiation is completely enclosed by perfectly reflecting walls, whether these be stationary or movable, the quantity N remains constant, whatever process may be considered. Thus if the process be one of free expansion from a smaller into a larger enclosure, neither u_ν nor ν changes, while in case the walls move, as in a Wien displacement, the Doppler effect produces for each type of light the same relative change in u_ν and ν.

Let us now consider radiation enclosed within mirror walls, one of which is so thin that, owing to random fluctuations in the pressure of the light, it acquires a sort of Brownian movement, until a stationary state is reached such that no further average exchange of energy between the thin wall and the radiation occurs. Even if the original radiation were monochromatic it would not remain so, but, owing to the Doppler effect produced by the vibrating wall, would become distributed over all frequencies from zero to infinity.

It remains to show that this stationary state is a state of true thermal equilibrium. Suppose that the outside of this wall is in contact with a gas which also by itself would give a Brownian movement to the wall. If the temperature of the gas is very high it will give to the wall more energy than it receives, and this in turn will be imparted to the radiation within the enclosure. If the temperature is very low the opposite process will occur. There will be one temperature of the gas when neither process will occur, on the average, and this may be defined as also the temperature of the radiation. We then evidently have a condition of thermal equilibrium such that by raising slightly the temperature of the gas we raise also that of the radiation, and this may be done in a perfectly reversible manner.

Thus the radiation may have any number of different states of equilibrium, all at the same temperature, according to the amount of energy originally in the enclosure, and only one of these states coincides with the state of black body radiation, which is alone considered in the classical thermodynamics of radiation.

It would seem that the only escape from the conclusion that more true equilibrium states really exist than have hitherto been considered would be to deny even the theoretical possibility of ideal mirror walls. But even this mode of escape fails, for we might consider a hollow of such enormous extent that it would take a very long time for any occurrence at the wall to affect the interior. If in such an enclosure we start with nearly monochromatic radiation and some free electrons, then there will be that interchange of energy and momenta between the electrons and the light which is known as the Compton effect, and this will result again in a stationary state in which the radiant energy is distributed between all frequencies

from zero to infinity. The temperature of such a state could be measured by the average kinetic energy of the electrons. Here also the process of reaching the equilibrium state will occur without change in the number of photons.

In all of these equilibrium states in which the number of photons is fixed we have in addition to equations (6) and (8),

$$\delta N = 0 \text{ or } \int_0^\infty \delta\left(\frac{u_\nu}{h\nu}\right) d\nu = 0. \tag{11}$$

If we now employ simultaneously equations (6), (8) and (11), the calculus of variations no longer shows that $\partial s_\nu/\partial u_\nu$ is a constant, but rather that

$$\frac{\partial s_\nu}{\partial u_\nu} = \lambda_1 + \frac{\lambda_2}{h\nu}, \tag{12}$$

where λ_1 and λ_2 are two undetermined coefficients which in a given thermal distribution are constant over the whole range of frequencies.

Instead of pursuing these purely mathematical methods to evaluate λ_1 and λ_2 we may treat the problem with greater simplicity by utilizing the fact that the thermal distribution in any system of radiation approaches as a limit, at high frequencies, the general equation first obtained by Wien (using an asterisk to denote equations true only in the limiting case of high frequency),

$$u_\nu = \text{const. } \nu^3 e^{-\frac{h\nu}{kT}}. \tag{13}^*$$

The constant of this equation was evaluated by Planck as $8\pi h/c^3$, but this gives only the particular kind of equilibrium known as that of black body radiation. In order to include all of our new types of equilibrium we may introduce a new quantity γ which is constant only when the number of photons is constant. If $\gamma = 1$ for the case of black body radiation, then in general γ will give the ratio, at any high frequency, between the actual energy density and the energy density in a black hollow at the same temperature. The general equation of the Wien type may then be written as

$$u_\nu = \frac{\gamma 8\pi h\nu^3}{c^3} e^{-\frac{h\nu}{kT}}. \tag{14}^*$$

The expression for the entropy of radiation, which was obtained in the preceding paper, and which is essentially identical with that of Planck, is

$$s_\nu = \frac{k\nu_\nu}{h\nu} \ln \frac{1}{8\pi\beta e} + \frac{8\pi k\nu^2}{c^3}\left[\left(1 + \frac{c^3 u_\nu}{8\pi h\nu^3}\right) \ln\left(1 + \frac{c^3 u_\nu}{8\pi h\nu^3}\right) - \frac{c^3 u_\nu}{8\pi h\nu^3} \ln \frac{c^3 u_\nu}{8\pi h\nu^3}\right] \tag{15}$$

from which, by differentiation and slight rearrangement, we find

$$\frac{\partial s_\nu}{\partial u_\nu} = \frac{k}{h\nu} \ln \frac{1}{8\pi\beta e} + \frac{k}{h\nu} \ln \left(\frac{8\pi h\nu^3}{c^3 u_\nu} + 1 \right). \tag{16}$$

For the limiting case of high frequencies this becomes

$$\frac{\partial s_\nu}{\partial u_\nu} = \frac{k}{h\nu} \ln \left(\frac{1}{8\pi\beta e} \frac{8\pi h\nu^3}{c^3 u_\nu} \right). \tag{17}*$$

Combining (14)* and (17)* we have

$$\frac{\partial s_\nu}{\partial u_\nu} = \frac{k}{h\nu} \ln \frac{1}{\gamma 8\pi\beta e} + \frac{1}{T}, \tag{18}$$

where we may dispense with the asterisk since this equation has the same form as (12) and since λ_1 and λ_2, being constant, have now been determined by finding their values in the range of high frequency.

Our problem is now solved, for we can equate the values $\partial s_\nu / \partial u_\nu$ given in equations (16) and (18), and find as our general expression for the distribution law

$$u_\nu = \frac{8\pi h\nu^3}{c^3} \frac{1}{\frac{1}{\gamma} e^{\frac{h\nu}{kT}} - 1}. \tag{19}$$

In the special case where $\gamma = 1$ this reduces to the familiar formula of Planck, but it also includes all the other states of true thermodynamic equilibrium that we have dealt with in this paper. We may note that for any value of $h\nu/kT$, as γ becomes smaller, equation (19) approaches equation (14)*, hence that generalized form of the Wien equation may be regarded as the universal law of radiation at small densities, just as the simple gas law is the limiting law for all gases at small densities.

All that I have attempted to show in this paper—and this I think I have shown beyond question—is that there are many states of radiation in thermal equilibrium which are not included in the classical thermodynamics of radiation, and that in these states the distribution of radiant energy with respect to frequency may be considered by methods similar to those that have been employed in the more limited fields previously studied.

It is true that I have been led to the discovery of these new equilibrium states through an attempt to find a law of conservation of photons, but their existence does not yet prove that such a law obtains. If it later proves possible to show that in absorption and emission of light the photon acts as an indestructible and uncreatable atom, then we shall find, not only in the thermodynamics of radiation, but also in the thermodynamics

of all substances, great fields of equilibria hitherto unsuspected, in which the individual states differ from one another with respect to the new variable, the number of photons. If such a necessity arises and the law of conservation of photons can be established, it may be necessary to revise still further our ideas of thermal radiation, for in that case it would be doubtful whether what is known as black body radiation is as definite a thing as has been supposed.

[1] Lewis, these PROCEEDINGS, **13**, 307 (1927).
[2] Lewis, *Nature*, **118**, 874 (1926).
[3] Einstein, *Ann. Physik*, **38**, 881 (1921); *J. Physique*, **3**, 277 (1913).

THE HYDROGEN ATOM WITH A SPINNING ELECTRON IN WAVE MECHANICS

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In this paper it is shown that the Schrödinger wave mechanics, plus the Uhlenbeck-Goudsmit spinning electron, completely represents the fine structure of hydrogen-like spectra.

The Hamiltonian function of the system in classical mechanics is taken as

$$H = \frac{1}{2m}\left[p_r^2 + \frac{p_\vartheta^2}{r^2} + \frac{p_\varphi^2}{r^2 \sin^2 \vartheta}\right] + \frac{1}{2I}\left[p_\theta^2 + \frac{1}{\sin^2\theta}\left(p_\Phi^2 + p_\psi^2 - 2p_\Phi p_\psi \cos\theta\right)\right]$$

$$- \frac{Ze^2}{r} + \frac{Q}{r^3}\left[\cos\alpha p_\vartheta p_\theta - \cot\theta \sin\alpha p_\vartheta p_\psi + \csc\theta \sin\alpha p_\vartheta p_\Phi + \cot\vartheta \sin\alpha p_\varphi p_\theta\right.$$

$$\left. + (1 + \cot\vartheta \cot\theta \cos\alpha) p_\varphi p_\psi - \cot\vartheta \csc\theta \cos\alpha p_\varphi p_\Phi\right] \quad (1)$$

in which r, ϑ, φ are polar coördinates of the center of the electron, referred to the nucleus (of atomic number Z); θ, ψ, Φ are Eulerian angles of the (spherical) electron referred to a parallel polar axis and initial plane; m is the mass of the electron, I its moment of inertia, e its charge, while $Q = \frac{Ze^2}{2m^2c^2}$, and α is an abbreviation for $\psi - \varphi$.

The writer has made use of the above expression for the quantization of the system on the old quantum theory;[1] the results were identical with those of other investigators.[2] It should be remarked that this form is valid only to terms of order v^2/c^2, where v is the velocity of the electron.

Further, the terms due to the relativity change of mass are omitted; it will be shown later that their inclusion leads to the addition of the Sommerfeld correction (with half-integral azimuthal quantum number k) to the energy.

To derive the corresponding wave equation we note that H is equal to the potential energy plus a quadratic form in the momenta. Introducing this quadratic form in Schrödinger's variation principle,[3] we obtain, neglecting terms of order Q^2 and higher,

$$\nabla^2 u + \frac{m}{I}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial u}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\left[\frac{\partial^2 u}{\partial\psi^2} + \frac{\partial^2 u}{\partial\Phi^2} - 2\cos\theta\frac{\partial^2 u}{\partial\psi\partial\Phi}\right]\right\}$$

$$+ \frac{2mQ}{r^3}\left\{\cos\alpha\frac{\partial^2 u}{\partial\vartheta\partial\theta} - \cot\theta\sin\alpha\frac{\partial^2 u}{\partial\vartheta\partial\psi} + \csc\theta\sin\alpha\frac{\partial^2 u}{\partial\vartheta\partial\Phi}\right.$$

$$+ \cot\vartheta\sin\alpha\frac{\partial^2 u}{\partial\varphi\partial\theta} + [1 + \cot\vartheta\cot\theta\cos\alpha]\frac{\partial^2 u}{\partial\varphi\partial\psi}$$

$$\left. - \cot\vartheta\csc\theta\cos\alpha\frac{\partial^2 u}{\partial\varphi\partial\Phi}\right\} + \frac{8\pi^2 m}{h^2}\left[E + \frac{Ze^2}{r}\right]u = 0. \quad (2)$$

We have to treat this by the method of perturbations.[4] Our perturbation is the term with factor $2mQ/r^3$. We put $u = au_0 + 2mQv$, $E = E_0 + 2mQ\epsilon$, where u_0 is a characteristic function of the unperturbed equation, and E_0 is the corresponding parameter.

The unperturbed equation corresponds to a spherical electron moving about the nucleus and simultaneously rotating, the two motions not affecting each other. A particular solution u_0 is then the product of the functions characteristic of these two motions. The first of these is well known.[5] The second is a special case of that worked out by Reiche and Rademacher.[6] The result is

$$\left.\begin{aligned} u_0 &= N\chi_{ne}(r)P_l^{n_1}(\cos\vartheta)T(\theta)e^{i(n_1\varphi + n_2\psi + n_3\Phi)} \\ T(\theta) &= \left(\sin\frac{\theta}{2}\right)^d\left(\cos\frac{\theta}{2}\right)^s F\left(-p, 1+d+s+p, 1+d, \sin^2\frac{\theta}{2}\right) \end{aligned}\right\} \quad (3)$$

where N is a normalizing factor, $\chi_{nl}(r)$ is Schrödinger's function for the quantum numbers n and l, $P_l^{n_1}$ is an associated Legendre function, and F a hypergeometric function. n is a positive integer; n_1, n_2, n_3, l, d, s, p are integers or zero; the four latter cannot be negative.

E_0 includes both orbital and spin energy. The latter is constant and does not affect the spectrum; it is proportional to $\sigma(\sigma + 1)$,[7] where

$$\sigma = \frac{1}{2}(d + s) + p.$$

We must take $\sigma = 1$. Moreover, $d = |n_2 - n_3|$, $s = |n_2 + n_3|$. This limits us to the following cases:

p	d	s	n_2	n_3	F
1	0	0	0	0	$\cos\theta$
0	2	0	± 1	∓ 1	1
0	1	1	0	± 1	1
0	1	1	± 1	0	1
0	0	2	± 1	± 1	1

We define

$$Y_l^{n_1}(\vartheta,\varphi) = P_l^{n_1}(\cos\vartheta)e^{in_1\varphi}, \quad Z_{n_3}^{n_3}(\theta,\psi,\Phi) = T(n_2,n_3,\theta)e^{i(n_2\psi+n_3\Phi)} \tag{4}$$

so that

$$u_0 = N\chi_{nl}(r)\,Y_l^{n_1}(\vartheta,\varphi)Z_{n_3}^{n_3}(\theta,\psi,\Phi). \tag{5}$$

After carrying out our substitutions on the wave equations (2) and performing several reductions, it takes the form.

$$\nabla^2 v + \frac{m}{I}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial v}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\left[\frac{\partial^2 v}{\partial\psi^2} + \frac{\partial^2 v}{\partial\Phi^2} - 2\cos\theta\,\frac{\partial^2 v}{\partial\psi\partial\Phi}\right]\right\} + \frac{8\pi^2 m}{h^2}\left[E_0 + \frac{Ze^2}{r}\right]V$$

$$= \frac{a}{r^3}N\chi_{nl}(r)X(l,n_1,n_2,n_3) - \frac{8\pi^2 m}{h^2}\epsilon a u_0. \tag{6}$$

$$\left.\begin{aligned}&\text{When } n_2 = \pm 1,\ X(l,n_1,n_2,n_3) = \pm\, y(n_2)\,Y_e^{n_1+n_2}Z_0^{n_3} - n_1 n_2 Y_l^{n_1}Z_{n_2}^{n_3}\\ &\text{When } n_2 = 0,\ X(l,n_1,o,n_3) = \pm\, y(-1)\,Y_e^{n_1-1}Z_1^{n_3} + Y_l^{n_1+1}Z_{-1}^{n_3}\end{aligned}\right\} \tag{7}$$

In general, $y(+1) = 1$, $y(-1) = (l-n_1+1)(l+n_1)$

but in some cases these values are to be divided by 2; their sign varies from case to case.

The general theory[4] shows that we can perform the following expansions:

$$\frac{N}{r^3}\chi_{nl}(r) = \frac{1}{r}\sum_{n'} A_{n'}\chi_{n'l}, \quad Nr\chi_{nl}(r) = \frac{1}{r}\sum_{n'} B_{n'}\chi_{n'l}$$

where the summation extends over all possible values of n', so that the right side of our equation can be expressed as the series

$$\frac{a}{r}\sum_{n'}\left[X(l,n_1,n_2,n_3)A_{n'} - \frac{8\pi^2 m}{h^2}\epsilon Y_l^{-n_1}Z_{n_3}^{n_3}B_{n'}\right]\chi_{n'l}.$$

X, in general, contains two terms, in one or both of which the indices of the functions Y and Z differ from l, n_1, n_2, n_3. If there is a term in X

in which these indices do not differ from l, n_1, n_2, n_3, there is then one term of the above expansion in which all five indices have the particular values n, l, n_1, n_2, n_3; and the theory[4] shows that the coefficient of this term must vanish. Since the coefficient of $Y_l^{n_1} Z_{n_1}^{n_2}$ in X is always $-n_1 n_2$, it follows that

$$\epsilon = -\frac{h^2}{8\pi^2 m} n_1 n_2 . \frac{An}{Bn} . \tag{8}$$

But if $n_2 = -1$ this is of precisely the same form as the result obtained by applying the same method of perturbations to the wave equation discussed by Professor Epstein,[5] which corresponds to a non-magnetic electron revolving about a nucleus containing a fixed magnetic dipole of moment Z times that of the spinning electron. This equation has been shown by Professor Epstein[5] to give the energy levels which, when added to the relativity correction (in the form for the new mechanics, with apparent half-quanta), produce the observed fine structure, on the assumption that the condition $n_1 = l + 1$ or $-l$ is satisfied.

Now, it can be shown by considerations too lengthy for inclusion here that we are actually restricted to the cases in which $n_2 = -1$ and $n_1 = l + 1$ or $-l$. Our wave equation thus gives the correct energy levels, provided that the relativity correction is additive; and this is now evident. For the characteristic function of the hydrogen-like atom without spin is affected by the relativity correction only in the form of the function $\chi_{nl}(r)$. We have made no use of the explicit form of this function, so that all our considerations still apply in the case including relativity; the energy terms which appear here as additive corrections will play the same part there.

With this the outline of the demonstration is completed; a more detailed account of the method will be published later. The writer wishes to express his deep indebtedness to Professor P. S. Epstein, whose constant advice and encouragement have made this work possible, and whose own investigations have contributed largely to its successful conclusion.

[1] *Physical Review*, **28**, 1926, p. 849 (Abstract). The same or an equivalent form has been used by others (see note 2). In a course of lectures recently delivered by Professor H. A. Lorentz at this Institute it was shown that this is not *strictly* the rigorous expression, since terms involving the accelerations are omitted. However, it is certain that within the approximation used (terms of order v^2/c^2) the rigorous expression leads to the same result. (In my equation, loc. cit., interchange j and k.)

[2] Heisenberg, W., and Jordan, P., *Zeits. Physik*, **37**, 1926, p. 263.

[3] *Ann. Physik*, **79**, 1926, p. 748.

[4] Cf. Schrödinger, *Annalen*, **80**, 1926, pp. 440ff; and for the method used here refer especially to Epstein, P. S., these PROCEEDINGS, **13**, June, 1927, p. 432.

[5] Schrödinger, *Annalen*, **80**, 1926, p. 479.

[6] *Zeits. Physik*, **39**, 1926, p. 444.

[7] *Ibid.*, p. 449.

[8] Epstein, P. S., these PROCEEDINGS, **13**, April, 1927, p. 232.